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Sampling and Analysis of Coke-Oven Door Emissions

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SAMPLING AND ANALYSIS OF COKE-OVEN DOOR EMISSIONS

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ABSTRACT

Emissions generated by leakage from a coke oven door were collected and sampled during a 16-hour coking cycle. Extensive analyses, including organic and bioassay analyses, were conducted on selected fractions of the emission samples.

A sealed-hood was fabricated to fit over the door of a coke oven so that gases leaking past the door during the coking cycle would be contained and representative samples could be obtained. Additional criteria for the hood included not severely altering the normal door leakage and not interfering with coke oven operation. Initial tests of one hood design suggested modifications which were incorporated into the final design. The final hood was used for conducting two sampling runs at an operating coke oven.

Analysis of the coke oven samples included:

1. Particulate emissions determination
2. Trace metal analyses
3. Gas analyses
4. Organic analyses by IR spectroscopy, GC-MS, TLC, and HRMS on entire samples or LC fractions of the samples
5. Bioassay analyses of bacterial mutagensis and mammalian cell cytotoxicity.

Results of the particulate mass emission determination show that a considerable variation can exist in emissions of coke ovens from cycle to cycle. Also, results of the bioassay analyses confirmed that the samples were mutagenic, as the chemical analyses would lead one to expect.

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SECTION 1

INTRODUCTION

In connection with a program to develop and evaluate concepts for minimizing emissions from coke-oven doors (EPA Contract No. 68-02-1439), Battelle's Columbus Laboratories (BCL) initiated development of a system for measuring these emissions. The basic equipment consists of a metal hood that extends over the buckstays adjacent to an oven door, thus capturing emissions from around the door and permitting these emissions to be channeled to an exit duct where they can be conducted to measuring devices.

The initial hood design was tested on a Koppers coke oven at Empire-Detroit Steel in Portsmouth, Ohio (see Appendix A, Figure 1). Although the system was judged to operate satisfactorily, it was believed that use of the sampling hood caused the oven door temperature to rise above normal, due to the hood eliminating natural convection currents that normally flow over the door and provide cooling.

To determine the amount of temperature rise above normal caused by the hood, an oven door at Portsmouth was instrumented with eight thermocouples and door temperatures were then measured throughout a complete coking cycle of approximately 15 hours (see Appendix A, Figures 2-8). A subsequent test with the sampling hood in place indicated a temperature rise above normal of about 28 C (50 F) during a 2-hour test. A heat transfer analysis made of the system showed that the temperature rise could be minimized by painting both sides of the hood black and installing vertical fins on the outside of the hood to enhance heat transfer from the hood to the ambient air.

Following this development work on the sampling hood, EPA authorized emission measurement tests to quantify particulate and gaseous emissions due to coke-oven-door leakage and to establish operating procedures and system reliability under real-life conditions. When these measurements were authorized, coke production at Portsmouth had been curtailed to the extent that samples could not be obtained from a representative coking cycle.

After delays while waiting for resumption of normal coke production at Portsmouth, it was decided to seek another test site. Republic Steel Corporation gave permission for emission measurement runs to be conducted at their Poland Avenue coke plant in Youngstown, Ohio. Two sampling runs were conducted at coke oven No. 41, Battery A, at this Republic plant during the week of March 29 through April 2, 1976.

During the test period, the following samples were collected:

1. Particulate samples; the samples were collected on a filter by using a Hi-Vol sampler.
2. Adsorbent column samples of volatile species; these were collected on a Tenax adsorbent column.
3. Flask samples for gas analysis

Extensive analyses were conducted on the samples collected from this test, as follows:

Sample	Analyses
Filter Samples	Mass, by drying and weighing
	Trace metals by spark-source mass spectroscopy
Extract of filter and adsorbent column samples	Level 1, by infrared spectroscopy
	Compounds by gas chromatography-mass spectroscopy
	BaP by thin-layer chromatography (EPA)
	Compounds by high resolution-mass spectroscopy (ERDA)
	Bacterial mutagenesis (Stanford Research Institute)
	Mamalian cell cytotoxicity (Northrup Services)
Gas Samples	Compounds by mass spec and GC

Analytical efforts were conducted by Battelle-Columbus, unless otherwise indicated.

This report describes the preparation leading up to the field test, conduct of the field test, and presents results of the analyses. Where possible, conclusions regarding the procedures used for sampling and analysis, and regarding the results of this test, are presented.

SECTION 2

GENERAL CONCLUSIONS

CONDUCT OF TEST

Sampling

Generally, the use of a finned hood over the door of a coke oven to contain door leakage gases and provide for sampling of these gases worked successfully in that samples were collected without damage to the coke oven or severe distruption to plant activities.

Improvements that should be considered for future efforts on sampling emissions from coke oven doors include:

1. Use of a larger blower so that more air could be fed into the hood. This would more accurately represent the normal air flow with a breeze, etc., and would provide better cooling of the oven door.
2. Redesign of the hood to permit insulating the outside surfaces to reduce condensation of volatile organics on the inside of the hood while providing adequate door cooling by increased air flow.
3. Insulation of ducts carrying gases withdrawn from the hood to reduce condensation.
4. Obtaining a continuous printout or, at least, frequent readings of air and gas flow rates so that leakage, etc., can be calculated. Because flow rates may change as filters become loaded, it is desired to obtain readings at intervals no greater than about 10 to 15 minutes early in the test. For the later stages of the test, hourly readings should surfice.
5. For a portion of a run, or for another trial of this hood system, it might be useful to add a tracer gas to the supply air so that leakage might be estimated more accurately.

6. To determine emission rates (mass of total particulate or certain compounds or elements per unit time), all material coming from the coke oven should be known. That would require collecting condensed material off of the inside of the hood and the gas ducts and attributing this material to the gas flow in some way. Three problems this introduces are (a) how to clean the hood and ducts safely when the residue being washed off may contain carcinogenic species, (b) how to clean the very large hood surfaces, and (c) how to equate the condensed mass to gas flow - obviously, more of the condensed mass would be collected early in the test.

The rather large differences in emission rates for the two runs on the same coke oven cell suggest that single tests will not be useful in precisely defining emissions from these sources.

Analysis

Due to the presence of large quantities of organics in the coke oven samples, and the increasing concern over health hazards related to organic materials, the possibilities for modifying or extending the analysis procedure are limited only by the imagination and the budget. Obviously, it would be desirable to conduct semiquantitation of all LC fractions of each sample. However, for this single test such an approach could have increased the number of GC-MS analyses to 88, rather than the 12 that were conducted. Also, for the semiquantitation analyses conducted there are significant unidentified fractions (e.g., 81 percent for Sample A1, Fraction 5) - of what does the missing material consist? Further, it might be desirable to conduct the HRMS, the trace metal analyses, and the bioassay analyses on LC fraction of samples, rather than on the entire samples. Again, material removed (in some future test) from the inside of the hood and gas ducts should be analyzed.

To facilitate interpretation of future test results, the quantity of sample used for all analyses should be precisely defined and blanks should be provided and run for all analyses.

INTERPRETATION OF RESULTS

Mass emissions from coke oven door leakage vary greatly over the cycle, ranging from over 1000 mg/min during the first hour to less than 1mg/min during the latter portion of the cycle. The fraction of the sample collected in the filter was about 90 percent for the first hour of Test 2, but dropped to about 45 percent for the period from about 8 hours to 13 hours into the test.

A major observation is the variation in mass emissions from one run to another. For example, the average mass emission rate for the first hour of the test was 410 mg/min, whereas, the mass emission rate during the same period for Test 2 was 1003 mg/min. These data suggest that the care taken in sealing the door can have a major effect on emissions, and that estimates of emission rates (or factors) based on a small number of runs could be inaccurate.

Chemical Analysis Results

The coke oven samples, as expected, were very complex mixtures of organic compounds. Even after separating the samples into 8 fractions by liquid chromatography (LC), the fractions were still complex mixtures. Because of the complex nature of the samples and the fact that several of the specifies identifications were of a qualitative nature, it is impossible to make exact comparisons of results achieved by the various chemical analyses. However, the LC fractions, the GC-MS analyses, and the HRMS analyses produced results that generally were consistent.

Significant emissions were found of several organic compounds that have been identified as carcinogenic, as follows:

benzo pyrenes
dibenzo anthracene
benzo phenanthrene
benzo anthracenes
benzo fluoranthenes
indeno pyrene.

The presence of these compounds is adequate to account for the positive bioassay results.

Bioassay Results

Complex mixtures such as the coke-oven samples submitted for biological analysis contain large numbers of materials which may be mutagenic, cytotoxic, or both. The chemical analysis of the samples indicated that mutagenicity was to be expected. The samples contained numerous polycyclic hydrocarbons which have been confirmed to be both mutagens and carcinogens. Benzo fluoranthene and benzo-a-pyrene are but examples.

Mixtures are always difficult to assay. Sometimes a sample may give a positive mutagenic response at one concentration but the mutation rate may fall off dramatically at the next higher concentration due to the toxic effect of the same material, or a second material effecting the mutagenesis of the first or the viability of the mutants. A large number of synergistic or antagonistic interactions may take place which can exaggerate or diminish net bioassy responses.

The fact that Ames assay found mutagens in all of the samples serves to confirm the chemical analyses. The samples were found to be moderately mutagenic at the very dilute concentrations analyzed. Thus the data really suggests that the particulates entrapped on the filters were heavily laden with mutagens when the total sample is taken into account.

In general, both the filter and the adsorbent column sample extracts showed a moderate but positive mutagenic response 0.5 μl of the sample. The 0.5 μl sample represents only 0.0007 percent of the extract of the filter which was submitted for bioassay analyses. The extract sample was obtained from one-eighth of the total filter area. When more of the sample extract was analyzed the mutagenic response was increased until the concentration was sufficient to elicit a toxic response. It thus becomes quickly apparent that the total sample contained thousands of times larger amounts of mutagenic substances.

It has been shown by Commonor[1] that the mutagenicity of a complex mixture of environmental pollutants can be the sum of the mutagenicity of the individual fractions. Such a possibility may account for the quantity of mutagenic substances in the filter samples. In this investigation it was ascertained that the quantity of benzo-a-pyrene (BaP) in the filter extract representing the first hour of the coking cycle was approximately 700 μg. The mutagenic detection level for BaP is approximately 1 μg per plate with the Salmonella tester strains. Therefore the BaP is present in the filter extract samples in 100 fold less concentration than the mutagens detected. Thus it is suggested that those mutagens which were detected were either present in much greater quantities than BaP, were mutagenic in significantly smaller quantities, or an additive effect of the total mutagenic compounds was operative, as Commonor suggests.

The results of the rabbit alveolar macrophage assay must be considered on a preliminary basis only. The particulate was unevenly distributed on the filter medium, due to uneven deposition aggravated by the loss of large quantities during transit. Thus, reliable representative quantitative samples could not be obtained. Clean unused filter media was not available as a control.

The relatively clean border of the filters was used and found to be nontoxic to the macrophages. The samples cut from the center of the filter media caused a significant reduction in cellular viability.

SECTION 3

SAMPLING PROCEDURES

SAMPLING EQUIPMENT

A new sampling hood with vertical corrugations acting as cooling fins, and black paint applied to both sides, was constructed for the tests at Youngstown, Ohio. The new features incorporated were a result of analytical and field work reported in Appendices A and B. After being checked out at BCL for satisfactory operation, the hood was taken to Youngstown and used for the program to measure emissions from a coke-oven door.

Figure 1* shows the sampling hood in place clamped to the buckstays on either side of the oven from which emissions were to be sampled. As shown in Figure 1 the hood consisted of 5 full sections and a single half section, all held together by piano-type hinges. On the back of each section, placed vertically along the edge, were magnetic tape strips which aid in maneuvering the hood into place and holding it to the buckstays. However, the magnetic strips were not capable of holding the hood firmly in place and preventing gas leakage. Special clamps attached to lengths of angle iron were used to firmly clamp each side of each hood section to the buckstay. All edges of the hood and the hinges were sealed with furnace tape and then further sealed with furnace cement to prevent leakage of gases out, or of air into, the cavity behind the hood. Also shown in Figure 1 is the layout of the sampling equipment on top of the coke-oven battery during the test.

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* Regulations at Republic in Youngstown prohibited the taking of any photographs at the test site. Therefore, Figure 1 is an artist's sketch showing the general layout of the sampling hood over a coke-oven door.

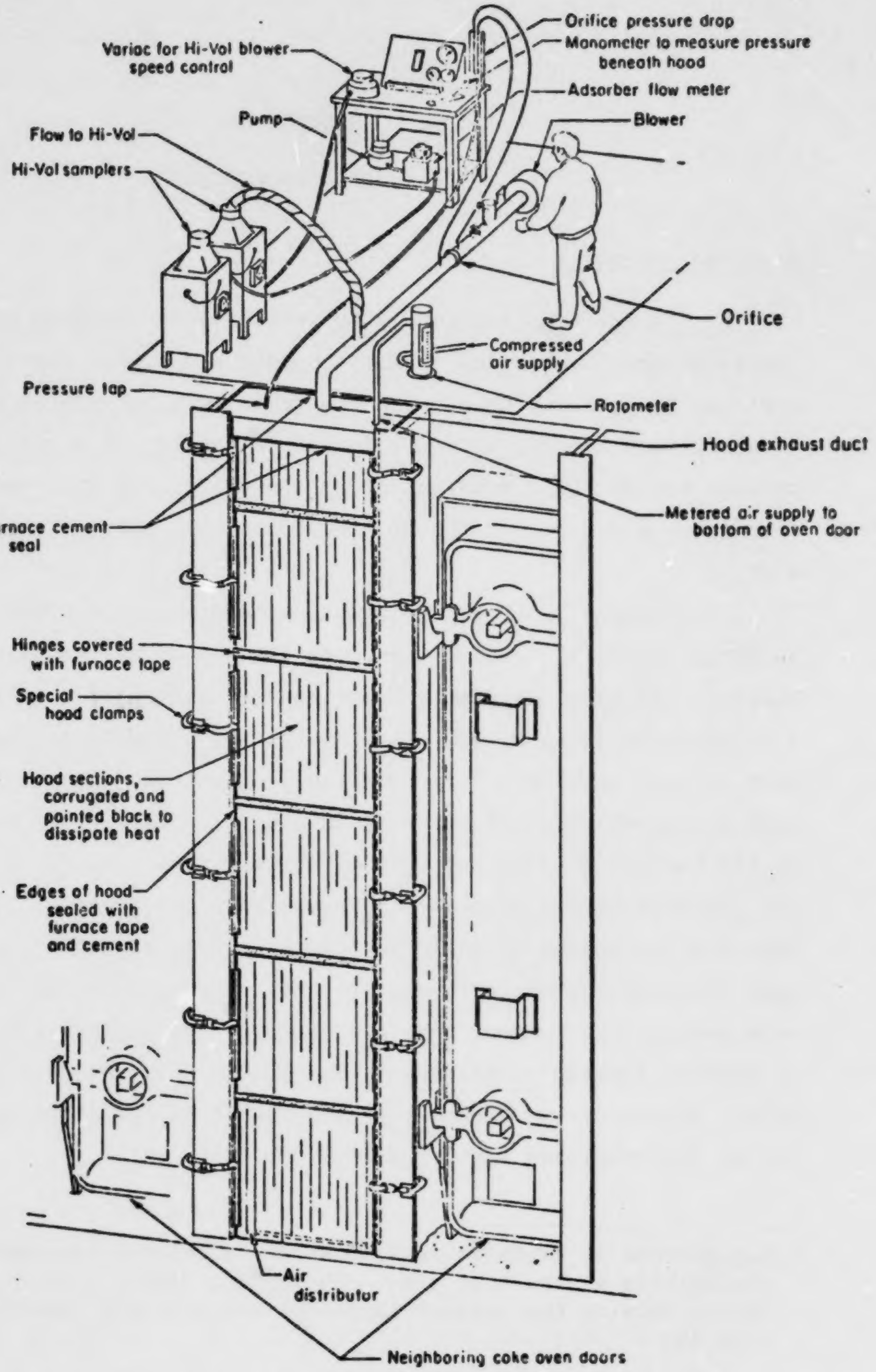
Orifice pressure drop
Manometer to measure pressure beneath hood
Variac for Hi-Vol blower speed control
Adsorber flow meter
Blower
Pump
Flow to Hi-Vol
Hi-Vol samplers
Orifice
Compressed air supply
Pressure tap
Rotometer
Hood exhaust duct
Metered air supply to bottom of oven door
Furnace cement seal
Hinges covered with furnace tape
Special hood clamps
Hood sections, corrugated and painted black to dissipate heat
Edges of hood sealed with furnace tape and cement
Air distributor
Neighboring coke oven doors

FIGURE 1. ARTIST'S SKETCH OF TEST EQUIPMENT ARRANGEMENT ON TOP OF OVEN NO. 41, "A" BATTERY - REPUBLIC STEEL CORPORATION, YOUNGSTOWN, OHIO

A supply of compressed air was delivered through a 1-inch pipe to a horizontal air distributor below the bottom of the oven door. The distributor consisted of a 1-inch diameter length of pipe with drilled holes that allowed air to blow upward over the door, mix with the door leakage gases, and pass on to the suction blower. The compressed air fed to the door originated from an air compressor. Ordinarily, a plant supply line could be used as the air supply, but at Youngstown it was necessary to rent a compressor for air supply because the plant compressed air supply system had excessive water in the lines. The compressed air supply to the hood was carefully metered by a rotometer.

The principle used to measure the leakage of emissions from around the coke-oven door was based on measurement of air fed under the hood and measurement of total gas flow away from the hood. This required that the blower draw gases away from the door area enclosed by the hood at the same rate as gases were generated by the air supply plus the door leakage, thus maintaining a zero gage pressure behind the hood. Positive pressure could cause leakage of gases from behind the hood and negative pressure could induce air leakage into the hood enclosure. As shown in Figure 1, a pressure tap was installed in the top plate seal, near the top of the buckstays. This pressure tap was connected to an inclined manometer sensitive to 0.001-inch of water, and efforts were made to keep the pressure reading on the manometer at zero to assure no leakage into or out of the door area. During the sampling period, the highest pressure differential recorded on the inclined manometer was 0.56 mm (0.022-inch) H_2O, and most of the time it was kept at zero. There was every indication that significant leakage did not occur during testing; all sealing materials were intact at the end of the test.

As a result of having the hood sealed in place and maintaining a zero pressure differential across the hood wall, all emissions leaking past the coke-oven door were induced to exit the hood through the duct identified in Figure 1 as "Hood exhaust duct". As the gases passed through this duct, part of the flow was pulled off by the Hi-Vol sampler; this part was measured and recorded at the Hi Vol. The remaining gases flowed on toward the blower and the flowrate was measured at an orifice mounted in the line. Thus, the gas flow measured at the Hi Vol plus the flow measured at the orifice gave the total flow being drawn from within the hood enclosure.

Between the orifice and the blower there was an adjustable valve which could be used to restrict the flow of gas going to the blower. Also between the adjustable valve and the blower, a tee was installed in the duct; one leg of the tee was an open leg which contained an adjustable butterfly valve. By opening the butterfly valve, unmetered air was drawn to the blower, thus reducing the quantity of gases pulled from the hood to the blower.

The capacity of the blower limited the amount of metered air that could be fed to the air distributor beneath the hood (even with the butterfly valve in the closed position). When the volume of metered air plus oven gas leakage from the door equaled the capacity of the blower plus the gas drawn to the Hi-Vol sampler, no more air could be supplied because the additional air would increase the pressure beneath the hood and cause leakage from beneath the hood.

It would be desirable that the blower have greater capacity so that much more air could be fed beneath the hood. Whereas the blower used for this effort had a capacity of about 300 m^3/hr (180 scfm), a capacity of at least 500 m^3/hr (300 scfm) would be desirable to provide additional cooling for the door. Also, the additional air would further dilute gases going to the Hi-Vol sampler which should cause less plugging of the filter on the Hi-Vol.

It was anticipated that filters on the Hi-Vol sampler might have to be changed frequently at the beginning of the coking cycle; therefore, two Hi-Vol samplers were provided. Quick connect and disconnect flexible duct connections were provided so that gas sampling could be quickly switched from one Hi-Vol to the other. In addition, to provide better chart records, each Hi-Vol was modified by installing a special motor giving one complete chart revolution per hour instead of the normal one revolution per 24 hours.

Figure 2 is a schematic diagram that shows the arrangement of the Hi-Vol sampler and related sampling equipment. Flow from the hood passed through the 0.20 x 0.25 m (8 x 10-inch) Hi-Vol filter. Downstream of the filter there was a tap which connected to an adsorber

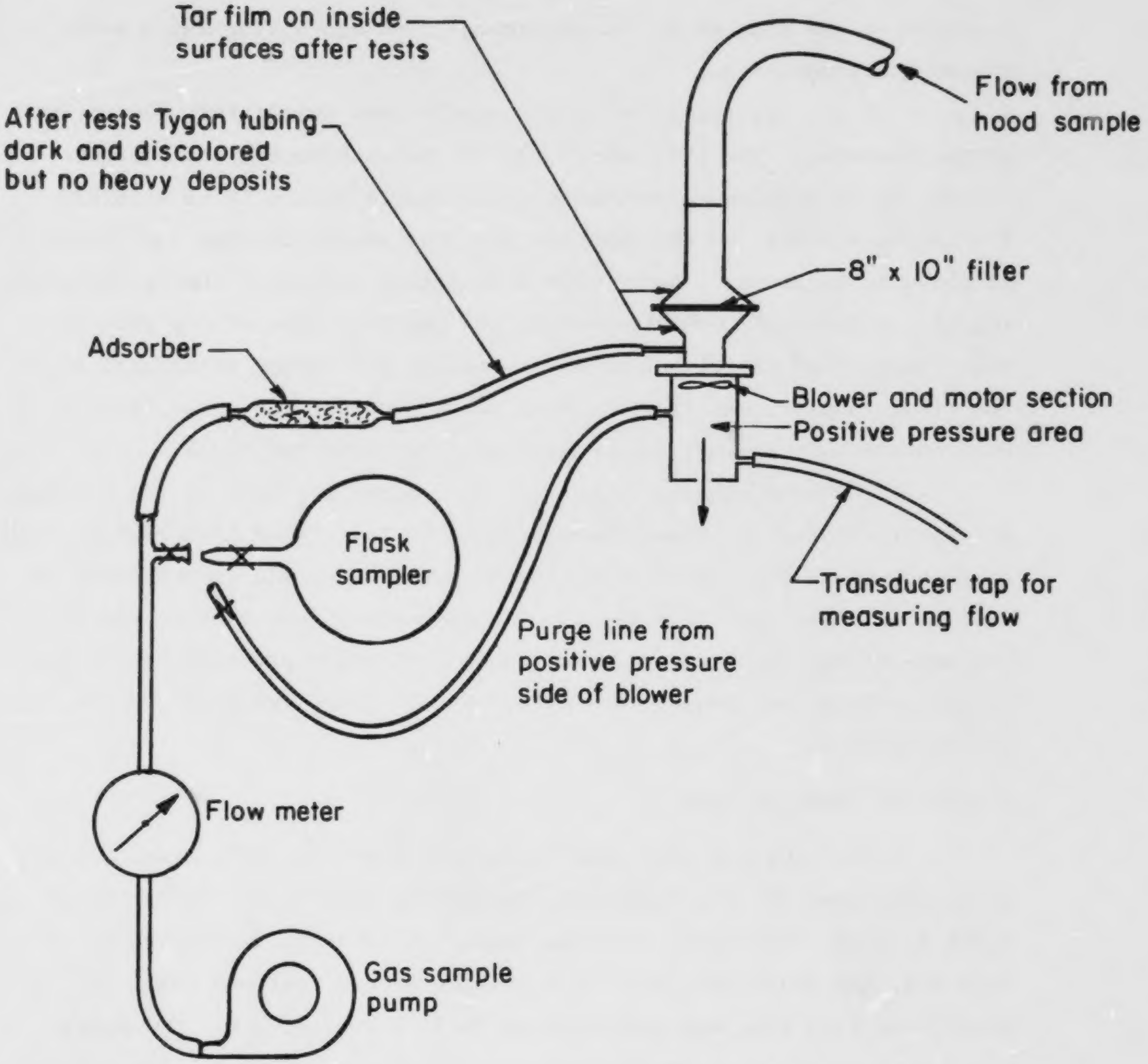
Tar film on inside surfaces after tests
Flow from hood sample
After tests Tygon tubing dark and discolored but no heavy deposits
8" x 10" filter
Adsorber
Blower and motor section
Positive pressure area
Flask sampler
Transducer tap for measuring flow
Purge line from positive pressure side of blower
Flow meter
Gas sample pump

FIGURE 2. SAMPLING ARRANGEMENT FOR PARTICULATE AND GAS SAMPLES

column, a dry gas meter or flow meter, and a gas sampling pump in that order. The adsorber column contained 35/60 mesh Tenax-GC, which has the capability of removing the heavy molecular weight hydrocarbons from a gas sample passing over it. After passing through the adsorber column, the gas passed through a dry gas meter which was used to measure the quantity of gas sampled by the adsorber column and a pump which maintained the sample flow.

A tee was installed in the sample line immediately downstream of the adsorber. The exit leg of the tee had a stopcock and a tapered fitting which enabled an evacuated flask sample bottle to be attached for taking a sample of the gas that has just passed through the adsorber. As shown in Figure 2, a purge line (consisting of rubber tubing terminating with a stopcock) was attached to the positive side of the blower-motor section of the Hi-Vol sampler. Before and during attachment of the flask sampler, gas from the hood was blown over the connections to help ensure that air was not collected in the sampling flask.

The hood-exhaust duct, from the top of the hood to the blower, was not insulated as it was thought that the relatively high flow through this duct would not result in excessive sample loss via condensation on duct walls. The line from the tie in the hood-exhaust duct to the Hi-Vol sampler was insulated. In retrospect, it would probably have been better to heat and insulate the entire duct between the hood and the Hi-Vol sampler.

CONDUCT OF SAMPLING RUNS

Two sampling runs were conducted at the Republic Steel Corporation Coke Oven No. 41, Battery A, during the week of March 29 through April 2, 1976. The first test was conducted on March 31, beginning at 3:10 a.m. and concluding at 6:45 p.m. The second test was begun on April 1 at 1:03 p.m. and completed on April 2 at 2:15 a.m. The second test was about 3 hours shorter than the first due to process demands; the coke was pushed after a shorter coking time.

No effort was made to select either a well-sealed or poorly-sealed door on which to conduct the test. Rather, the intent was to sample a "typical" door. A coke oven near the end of the battery was selected for the test to minimize the disruption of the test due to plant equipment moving past the sampling area.

The operation of an individual coke oven at this plant is approximately as follows:

- push previous charge
- oven remains open for 5 to 15 minute interval
- put door in place
- charge oven with fresh coal (up to 5 minutes)
- seal charging doors
- coking period of 12 to 16 hours
- doors removed for 15 to 30 minute interval prior to push
- push coke (about 2 to 3 minutes)

The hood was put in place and sampling begun as soon as possible after the door was closed. Thus, sampling was begun during the charging operation, but did not include the entire charging period. Sampling was continued until about 15 to 30 minutes before the end of the coking cycle. Sampling was stopped to allow sufficient time to remove the hood and sampling equipment before coke pushing was to begin.

Prior to sampling runs, it was empirically decided that the coking cycle of approximately 16 hours should be divided into time segments for purposes of taking samples for analysis. The length of these six sampling segments were assigned as follows:

Segment No.	Length of Segment, hours
1	1
2	1
3	2
4	4
5	4
6	4

Length of the segments was based on the knowledge that emissions from coke oven doors decreased as time into the cycle increases. Therefore, to obtain suitable sample quantities for analytical purposes, longer sampling times are required as the coking cycle progresses. A flask sample was planned midway through each of the six segments designated; thus, flask samples were taken at about 0.5, 1.5, 3, 6, and 10 hours elapsed time and at some convenient point during the last sampling segment.

Concerning the sampling and deposits on the duct, some deposits were observed on all of the duct with the heaviest deposits being found on the duct between the tee and the blower. It was noted that the temperature drop from the hood exit to the Hi-Vol sampler did not exceed 93 C (200 F). The Hi-Vol filter temparature was 82 to 107 C (180 to 225 F) during the sampling period.

CONDITION OF SAMPLING EQUIPMENT AFTER TWO TESTS

At the conclusion of the two Youngstown tests, the five full sections of hood subject to direct radiant heat from the oven door were covered with a thin coat of black tarry material giving the appearance of a coat of black spray paint. The top hood section, about half the height of other sections and subject to less radiant heat, had a thicker coat of tar appearing more like a brush coat of black paint.

The metal lid that covered the top of the buckstays had a thick paint-like coat of tar with a run buildup around the gas exit hole.

The 4-inch flexible duct leading from the buckstay lid to the metal ductwork contained a progressively heavier coating from beginning to end, with the exit end having a coating like shiny, heavy black lacquer.

The 2-inch flexible duct leading to the Hi-Vol sampler contained progressively heavier tar deposits with run deposits up to 1/16-inch thick at the exit end.

The sampler metal cap upstream of the filter had an inside coating appearing as a heavy black spray paint.

Tygon tubing that carried gas samples from downstream of the filter to the adsorber column had some discoloration but not the deposit evidenced in other parts of the system.

The metal surface of the sampler downstream from the filter had some deposit similar to very light spray paint.

The 4-inch metal duct leading to the exhaust fan had heavy deposits like brushed paint. When the fan was laid on its side after tests, with an approximately 6-foot-long metal duct projecting vertically upward, tar deposits 1/16-inch thick were formed on the fan parts from warm tar dripping from the duct walls.

COMMENTS ON SAMPLING PROCEDURE

In general, the sampling hood and associated sampling equipment performed satisfactorily during the two Youngstown tests. The one equipment weakness at Youngstown was in the exhaust blower that pulled the gases from behind the sampling hood. A greater blower capacity would permit a larger flow of air to be passed over the oven door for cooling purposes, and more dilution of leakage gases would reduce rapid filter loading. Also, heating and insulating the duct between the hood and the tee would reduce loss of condensibles.

The intent of the sampling system that was used was to provide a constant flow at the Hi-Vol sampler and at the POM sampling point. Fluctuations in gas leakage would be compensated for by adjusting the butterfly valve controlling bleed air to blower system. An alternative would have been to sample particulate (and POM) from the duct to the blower and to have omitted the Hi-Vol sampler. However, to do this, the sampling rate would have to be adjusted to provide isokinetic sampling with changes in air flow rate. The latter system would be slightly more cumbersome to operate, but, theoretically, would provide a more logical sampling procedure in that sample collection rate would match leakage rate.

SECTION 4

ANALYTICAL PROCEDURES

This section of the report describes the procedures used to analyze the samples obtained during the sampling effort conducted on the Republic Steel Corporation coke oven. Initial analysis conducted on the coke-oven samples was a gravimetric determination of the mass collected on the filters. Subsequently, the extract from the filters and the adsorbent samples was subjected to a number of detailed analyses related to determining the environmental hazard of coke-oven emissions.

Because Test 2 contained 4.1 times the particulate concentration as Test 1 and a more accurate recording of test parameters was made, Test 2 was chosen as the test run to be analyzed. Table 1 identifies the filter and adsorber column samples for Test No. 2. The sample numbers shown in Table 1 are used in reporting most of the analytical results.

TABLE 1. IDENTIFICATION OF TEST NO. 2 SAMPLES

Sampling Time	Filter Nos.	BCL Code	Adsorber Nos.	BCL Code
1303-1411	119-131	A1F	2.1, 2.2	A1
1414-1506	132-136	A2F	2.3, 2.4	A2
1506-1708	137-147	A3F	2.5, 2.6	A3
1708-2105	148-155	A4F	2.7, 2.8	A4
2105-0215	156-161	A5F	2.9, 2.10, 2.11	A5
Compressor air supply (Blank)	--	--	TP.4	A6

Section 5 presents the results obtained in conducting the analyses described in this section.

MASS DETERMINATION

The mass of deposit collected on the filters was determined by desiccating the filters for 24 hours and then weighing them. Tare weights of the desiccated filters were subtracted from the final values to determine the mass of material collected.

To the extent possible, the samples were stored in a cooled dark location prior to analysis. Desiccation and weighing were conducted at room temperature, and the weighing was done in the presence of light. However, the precautions taken should have protected most compounds from photo reaction.

PREPARATION OF ADSORBENT COLUMN AND FILTER SAMPLES

From the group of filters representing a portion of a specific run, each filter was divided into quarters using a long-bladed lab spatula. Filters to be used for certain analyses were not to be extracted; these filter portions were set aside. The remaining filter sections were Soxhlet extracted sequentially with methylene chloride and methanol until the solvent around the Soxhlet thimble remained clear (approximately 3 days). Extracts were combined and reduced in volume. The extracted samples were then divided and, together with the filter sections that had not been extracted, were distributed to Battelle (BCL), U.S. Bureau of Mines (USBM), and EPA as follows:

- BCL (Organic) 1/4 of each filter group, extracted as above.
- BCL (Inorganic) 1/4 of each filter group, no extraction.
- USBM (Organic) 1/4 of each filter group, extracted as above.

- EPA (Bioassay) 1/8 of each filter group, no extraction;*
  1/8 of each filter group, extracted as above

The Tenax-GC adsorbent columns were Soxhlet extracted with pentane for a period of 24 hours. The appropriate extracts were combined, reduced in volume and one-fourth of each extract was distributed as follows:

BCL for organic analysis by Level 1 and GC-MS
EPA bioassay analysis by Ames (mutagenicity) and Ram
  (cytotoxicity) tests
USBM for Organic Analysis by HRMS
BCL saved for possible future analysis

LEVEL 1 TYPE ORGANIC ANALYSIS

Level 1 organic analysis was conducted on each set of filters and adsorbent column samples using the analysis procedure described in the EPA publication listed as Reference 2. The objective of this Level 1 analysis is to semiquantitate the predominant classes of organic compounds present. This is achieved by subjecting the extracted sample to liquid chromatography (LC) using solvent gradient elution. Each sample is separated into eight fractions containing different organic classes which may present. Because of the large amounts of material collected on the 0.20 x 0.25 m (8 x 10 inch) filter, only 1/600 (0.25 ml) of the sample was used for liquid chromatography. All the material extracted from the adsorbent columns was subjected to this analysis.

Gravimetric Analysis

Following liquid chromatography, the solvent was evaporated from each fraction in air until a constant weight was achieved. After recording the weights, the fractions were redissolved in methylene chloride prior to analysis by infrared spectroscopy. Results are reported in Table 5.

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*Following removal by EPA of small segments for the cytotoxicity tests the filter group was extracted with cyclohexane for BaP analysis.

Infrared Spectroscopy

Infrared spectra were obtained on the eight liquid chromatographic fractions of each of the 11 samples. The samples were prepared for the infrared analysis by depositing a film (from Me_2Cl_2 solutions) of each fraction on an infrared transmitting (KBr) crystal. The spectra were obtained using a Fourier Transform infrared (FT-IR) system. FT-IR systems use an interferometer (instead of a monochromator) to generate the spectral data in terms of an interferogram. A dedicated computer then makes the Fourier Transform of the interferogram (light intensity versus time) to the more usable infrared spectrum (light intensity versus wavelength). The sensitivity of the interferometer coupled with the data handling capability of the dedicated computer are two of the advantages of FT-IR systems over conventional dispersive infrared spectrophotometers. The use of FT-IR systems is not a normal part of Level 1 type analysis, but the ability to subtract spectra (see subsequent discussion) provides qualitative identifications that are not possible without this capability.

The liquid chromatographic separation roughly separates the samples into classes or types of compounds, but each class is still a complex mixture of many compounds. Since resolution is not sufficient to isolate individual compounds, it is extremely difficult to identify individual compounds by IR, or even distinct compound types. However, by using FT-IR (with the capability to subtract the spectra of consecutive fractions), such specific identifications are possible.

GAS CHROMATOGRAPHY-MASS SPECTROSCOPY ANALYSIS OF SELECTED SAMPLES

Following infrared analysis of the 88 sample fractions, representative filter and adsorber samples from each LC class fraction were chosen to undergo further analysis using gas chromatography-mass spectroscopy (GC-MS) to obtain a semiquantitation of the amount of various species present. The GC-MS semiquantitation procedure used was similar to procedures described in Reference 2. The samples were chosen on the basis of their representation of the classes of compounds found to be common in each class fraction as determined by IR. Whenever IR indicated any difference in these class fractions, these differing samples were also subjected to GC-MS. Fractions selected for GC-MS are indicated with an asterisk in Tables 6 and 7.

Gas chromatography separation was carried out using a 1.8 m (6-ft), 3 percent OV-101 column programmed from 70 to 300 C at 4 C min^{-1}. Both, chemical ionization (CI) and electron impact (EI) mass spectra were obtained using a Finnigan 3200 quadrupole mass spectrometer.

CI mass spectra were obtained using methane as the reagent and GC carrier gas. The mass spectra thus obtained are usually characterized by a prominent protonated molecular ion (M+1) together with adduct ions at (M+29) and (M+41) due to the addition of C_2H_5 and C_3H_5 in the mass spectrometer. The advantage of CI mass spectrometry is that it is usually possible to obtain reliable molecular weight data on unknown compounds. Since CI is a relatively low-energy process compared to EI, it generally produces less fragmentation which is characterized by the loss of neutral molecules and relatively stable ions.

EI, while less sensitive than CI, is the most common method for obtaining mass spectra. Since EI is a higher energy process, it produces more fragmentation giving rise to a more unique mass spectrum for any compound and, thus, is more useful for spectra matching. Reference mass spectra are usually available using the EI mode.

Mass spectral interpretation was further aided by a spectral matching routine whereby EI mass spectra are compared directly with more than 30,000 known spectra in the Battelle mass spectral data bank. The 10 best spectral matches are printed out based on a dissimilarity index of the fraction of unmatched intensities. Compound matches with a dissimilarity of 0.3 or less and with concurrence of the reference spectrum from an 8-Peak Spectral Index were considered to be identified with a high degree of certainty.

Following EI and CI GC-MS analysis, the individual components in each fraction were assigned structures on the basis of CI molecular weight determinations and fragmentation patterns, and on the basis of EI reference spectra and spectral matching. Where several structural isomers were possible, no attempt was made to identify each isomer since this was believed to be beyond the scope of this work. A tabulation of the compounds identified in each sample examined is given in Table 8 in Section 5.

Semiquantitation for the identified GC-MS components were achieved by ratios of the sum of all measurable peak heights in a given sample to the height of the known GC component. The ratio was then multiplied by the total amount of material in the fraction. Whenever an identified component did not exhibit an easily measurable GC peak, the reconstructed gas chromatogram was expanded. The expanded GC component area was then measured, divided by the amount of expansion and proportioned by the sum of the total peak heights as obtained before expansion. This ratio was then multiplied by the total amount of material in the fraction as above.

This semiquantitation procedure assumes that all the components in a given sample pass through the GC column and that they are recorded as a measureable peak in the gas chromatogram. Although this requirement is not always met, the procedure will give an indication as to the relative amounts of each species present in a given sample.

The results of the semiquantitation analysis are presented in Table 9 of Section 5.

ANALYSIS BY THIN LAYER CHROMATOGRAPHY

Quantitation for benzo-a-pyrene only was performed by Dr. Joseph Bumgarner (EPA) on the filter extracts using thin layer chromatography (TLC). These filter extracts were prepared by Dr. Bumgarner by extracting filter portions designated for cytotoxicity testing.* Very small segments were first removed for the cytotoxicity work; the remainder was then extracted with cyclohexane. The TLC plates were scanned using a Perkin-Elmer MPF-3 fluorescence spectrophotometer for benzo-a-pyrene using an excitation wavelength of 388nm and read at an emission wavelength of 430nm.

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*See Mannalian Cell Cytotoxicity write up (p.28) for description of condition of samples.

Recovery studies based on spiked blanks showed an average recovery of 98.9 ± 5 percent. The limit of detection is 0.1ng based on the standard of a peak being twice the background.

ANALYSIS BY HIGH RESOLUTION MASS SPECTROMETRY

High resolution mass spectrometric (HRMS) analyses were conducted on 1/4 of the methylene chloride filter extracts and 1/4 of the adsorbent sampler extracts. This work was performed by Dr. A. G. Sharkey of the U. S. Energy Research and Development Administration.

Low voltage mass spectrometry was initially performed on all samples to identify the molecular ions prior to analyses by HRMS.

TRACE METALS ANALYSIS

The elemental composition of emissions from coke oven doors was determined by spark-source mass spectroscopy (SSMS) of samples from Test No. 2. To make this analysis, the 1/4 portions of unextracted 8" x 10" filters and of a blank filter were subjected to SSMS.

Each of the fiber glass filter samples (A1F through A5F) and blank (A6F) were extracted in hot $HCl \cdot HNO_3$. The extract which contained the collected sample as well as some dissolved fiber glass was taken to dryness and mixed with graphite in the weight ratio of 3 sample to 1 graphite. The graphite is added to provide electrical conduction and to aid in forming a sound sample briquette for analysis by SSMS.

Standardization of SSMS was carried out by comparing the SSMS data with data for high concentration elements from analysis by optical emission spectroscopy.

Additionally, SSMS was conducted on 100 mg of coal and coke as obtained from the Youngstown facility. These analysis were conducted similarly to that of the glass filter samples above.

ANALYSIS OF FLASK SAMPLES OF GASES

All samples were analyzed on an "as received" basis by the mass spectrometer to provide information on mass to charge ratio of 1 through 100. Each sample was then analyzed by gas chromatography using both a thermal conductivity detector and a flame ionization detector. Sample No. 1, Test No. 2 was concentrated by using a liquid nitrogen trap to remove the noncondensables while pumping to approximately 2 torr pressure. This concentration step removes oxygen, nitrogen, argon, methane, and carbon monoxide and leaves the condensable compounds in the trap. The trap is then warmed to evaporate the condensables and condensables are analyzed by mass spectrometry. This concentration step increases sensitivity and accuracy of analysis for C_5 to C_7 hydrocarbon compounds. As the hydrocarbon detected using the concentration step were not significantly greater than without this step, it was not included in the analysis procedure for remaining samples.

The specific gases identified by each technique is as follows:

Mass spectroscopy

- -nitrogen
- -oxygen
- -argon
- -carbon dioxide
- -hydrogen
- -benzene
- -toluene

Gas chromatography-thermal conductivity detector

- -carbon monoxide
- -methane

Gas chromatography in flame ionization detector

- -acetylene and ethene
- -ethane
- -propene
- -propane
- -1-butene
- -iso-butane
- -n-butane

These techniques are sensitive to about 50 ppm, 10 ppm, and 0.1 ppm, respectively.

BACTERIAL MUTAGENESIS BIOASSAY

Stanford Research Institute examined seven coke-oven samples (A1F, A3F, A5F, A1, A3, A5, and A6) for their potential bacterial mutagenesis. The assay was conducted according to the recommendations of Ames using four of his testor strains with and without the rat liver microsome induced system. Each sample was examined twice on separate days by a single plate incorporation dose response assay. The following was transcribed directly from their report to EPA (Ref.5) with only minor format changes to conform with the rest of this report.

The Salmonella typhimurium strains used were all histidine auxotrophs by virtue of mutations in the histidine operon. When these histidine-dependent cells are grown on a minimal media petri plate deficient in histidine, only those cells that revert to histidine independence (his^+) are able to grow (mutants). The spontaneous mutation frequency of each strain is relatively constant, but when a mutagen is added to the agar the mutation frequency is increased 3 to 100 times. In addition to having mutations in the histidine operon, all the indicator strains have mutations in the lipoplysaccharide coat ($\underline{rfa}^-$) and deletions that cover a gene involved in the repair of uv damage ($\underline{uvrB}^-$). The $\underline{rfa}^-$ mutation makes the strains more permeable to large molecules, thereby increasing their sensitivity to these molecules. The $\underline{uvrB}^-$ mutation decreases repair of some types of chemically damaged DNA and thereby enhances sensitivity to some mutagenic chemicals. Strain TA1535 is reverted to histidine prototrophy (his^+) by many mutagens that cause base-pair substitutions. TA100 is derived from TA1535 by the introduction of the R factor plasmid pKM101.[3] The introduction of this plasmid, which confers ampicillin resistance to the strain, greatly enhances the sensitivity of the strain to some base-pair substitution mutagens. Mutagens such as benzyl chloride and 2-(2-furyl)-

3-(5-nitro-2-furyl) acrylamide (known as AF2) can be detected in plate assays by TA100 but not by TA1535. The presence of this plasmid also makes strain TA100 sensitive to some frameshift mutagens--e.g. ICR-191, benzo-a-pyrene, alfatoxin B_1, and 7,12-dimethylbenz-a-antracene. Strains TA1537 and TA1538 are reverted by many frameshift mutagens. TA1537 is more sensitive than TA1538 to mutation by some acridines and benzanthracenes, but the difference is quantitative rather than qualitative. TA98 is derived from TA1538 by the addition of the plasmid pKM101, which makes this strain more sensitive to some mutagens.

For each experiment, an inoculum was taken from a frozen repository (-80°C), grown overnight at 37°C in a nutrient broth consisting of 1 percent tryptone and 0.5 percent yeast extract. After stationary overnight growth, the cultures are shaken for 3 to 4 hours to ensure optimal growth. Each culture was checked for sensitivity to crystal violet. The presence of the $\underline{rfa}^-$ mutation makes the indicator strains sensitive to this dye, whereas the parent strain, $\underline{rfa}^+$, is not sensitive to the dye. However, the mutation is reversible, leading to the accumulation of $\underline{rfa}^+$ cells in the culture. Therefore, the cells must be tested routinely to ensure their sensitivity to crystal violet. Each culture also was tested by specific mutagens known to revert each test strain (positive controls).

Some carcinogenic mutagens (e.g., dimethylnitrosamine) are inactive unless the bacteria strains are converted to their active form by being metabolized. Ames has described the metabolic activation system used.[3,4] Adult male rats (250 to 300 g) are given a single 500 mg/kg intraperitoneal injection of a polychlorinated biphenyl (Aroclor 1254). Four days after the injection, the animals' food was removed. On the fifth day, the rats were killed and the liver homogenate prepared.

The assay itself was conducted in the following manner. To sterile 13 X 100mm tubes containing 2 ml of 0.6 percent agar containing .05 mM histidine and .05 mM biotin were added in order

0.05 ml of indicator organisms
0.5 ml of metabolic activation mixture (when used)

Up to 50 µl of a solution of the test chemical.

This mixture was stirred gently and then poured onto glucose minimal agar having the following composition:

15 g of agar, 20 g of glucose, 0.2 g of $MgSO_4 \cdot 7\ H_2O$, 2 g of citric acid monohydrate, 10 g of K_2HPO_4, and 3.5 g of $NaHNH_4PO_4 \cdot H_2O$ per liter.

After the top agar had solidified, the plates were incubated at 37C for 2 days.

The number of $\underline{his}^+$ revertants is counted and recorded. Some of the revertants are routinely tested to confirm that they are $\underline{his}^+$, require biotin, and are sensitive to crystal violet ($\underline{rfa}^-$).

All of the samples were analyzed as they were received. Dilutions of the samples were made in dimethylsulfoxide (DMSO). The amount of sample added per plate is expressed as the µl of sample in 50 µl of DMSO. The results of these investigations are reported in Tables 19 and 20 (Presented in next Section).

MAMMALIAN CELL CYTOTOXICITY

Preliminary cytotoxicity testing of filter samples A1F, A2F, A3F, A4F, and A5F was preformed by Northrup Services utilizing cultured rabbit alveolar macrophages[6]. The filter segments as received had suffered some degradation as a result of handling and shipping. Some of the particulate material had flaked off the filters and was lying loose in the containers. As is often the case in filters collected in the field, the particulate was not evenly distributed all over the surface of the filter. This situation was aggravated by the loss of some of the particulate. An attempt was made to remove the particulate from the filter however, it was impossible to do this without also removing some of the filter fibers that were imbedded in the particulate, thus it was decided that the test would be conducted by removing squares of material from the filters and utilizing these squares in the test. Therefore, small, medium, and large squares were removed from each filter in an effort to develop a dose response. However, due to the heterogeneous distribution of particulate on the filters, the dose response data generated are highly questionable and are not reported.

No control filters were provided which lead to the decision that the relatively clean edge of each filter would be removed and used as a control.

SECTION 5

RESULTS

Test No. 1 was in some ways a preliminary test, in that problems in recording data, changing filters and adsorbers, and in recording flows could not be anticipated as they could for Test No. 2. Test No. 2 was better organized and the various flows were more accurately recorded; therefore, of the two tests completed at Youngstown, Test No. 2 (on April 1-2) was chosen for the more complete analysis, including particulate mass and gas analysis and, in most instances, the data obtained in Test No. 2 are used in presenting results.

Although the two sampling runs were made on the same oven, the concentration of emissions was greatly different for the separate runs made only about a day apart. Test No. 2 showed an overall particulate emission rate about three times that measured in Test No. 1, and total light hydrocarbon concentrations about two times as great as measured for Test 1. The fact that such wide variations in emissions occur on a single oven served to illustrate the wide range that can exist between emissions data obtained on different coke ovens.

DOOR LEAKAGE AND FLOW DATA

Table 2 gives a summary of flow data taken at irregular periods throughout Test No. 2. Test No. 2 started at 1303 April 1, and Table 2 shows that leakage was relatively high around the door with a value of 99 m^3/hr (58 cfm), at 1320, or 17 minutes later. Theoretical calculations indicate that if an 0.8 mm (1/32-inch) crack is present around half of the perimeter of a door 4.1 m (13.5 ft) high and 0.7 m (2.25 ft) wide, leakage would be 217 m^3/hr

TABLE 2. TEST NO. 2 FLOW FOR AIR INPUT, HI-VOL SAMPLER, AND DUCT ORIFICE

Date and Clock Time	Hood Air Input (Rotometer Flow), scfm[a]	Orifice Gas Flow, scfm	Hi-Vol Sampler Flow: Uncorrected, scfm	Hi-Vol Sampler Flow: Corrected,[b] scfm	Coke Oven Door Leakage[c]: scfm(c)	Coke Oven Door Leakage[c]: m^3/hr
4/1-1320	14.5	47.6	29.2	24.5	58	99
4/1-1600	37.3	49.0	15.6	13.1	25	42
4/1-1737	41.0	50.5	16.0	13.4	23	39
4/1-1910	41.0	45.8	26.3	22.2	27	46
4/1-2237	41.0	46.8	30.7	25.8	32	54
4/2-0203	41.0	45.8	30.0	25.2	30	51

(a) At 29.92" Hg and 70 F
(b) Net flow is gross Hi-Vol corrected for calibration factor.
(c) Door leakage = Hi-Vol flow + Orifice flow - Hood air input.

(128 ft^3/min^*), assuming a gas pressure of 8 mm H_2O in the oven, and a gas temperature at the crack of 316 C (600 F). Table 2 shows that leakage had declined to 42 m^3/hr (25 ft^3/min) about three hours after the start of the test, leakage remained in the range of 39 to 54 m^3/hr (23 to 32 ft^3min) for the remainder of the test.

PARTICULATE MASS EMISSIONS

Although adsorber flows and overall data from Test No. 1 were not as accurate as Test No. 2, filter weights and flows from the Hi-Vol samplers were available. Accordingly, Table 3 summarizes the filters and their weights, and the flow of gases through the filter from Test No. 1.

Table 4 summarizes filter weight and flow data from the Hi-Vol samplers for Test No. 2. Door leakage in Test No. 2 was much greater than the door leakage in Test No. 1. Table 3 shows that Test No. 1 required 18 filters

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* Gas pressure = 8 mm = 0.011 psi; temperature at leakage point = 600 F
Area of opening around door = (27 + 4.5) x 1/32 x 1/12 x 1/2 = 0.04 ft
Gas density ρ = 0.075 x (460 + 70)/(460 + 600) = 0.0375
Then velocity V = 96.3 x (0.011/0.0375) = 52.2 ft/sec
and volume Q + AV = 0.041 x 52.2 x 60 = 128 ft^3/min.

TABLE 3. SUMMARY DATA, NO. 1 TEST, COKE OVEN DOOR LEAKAGE
REPUBLIC STEEL, YOUNGSTOWN, OHIO 4/1-2/76

Clock Time		Approximate Hours Into Test	Filter Number	Average Uncorrected Filter Flow As Recorded on Hi-Vol Chart, cfm(a)	Corrected Filter Flow, scfm(b)	Filter Flow With Hi-Vol Calibration Correction, scfm(c)	Dilution Correction Factor(d)	Net Leakage Flow Through Hi-Vol, scfm	Time of Flow Through Filter, minutes	Total Time, minutes	Leakage Flow Through Filter,	
On	Off										ft^3	m^3
3:10	3:21		100	32	24	24	.58	14	11	11	154	4.361
3:21	3:30		101	34	26	22	.57	13	9	20	117	3.313
3:30	4:12	1	102	38	29	29	.61	18	42	62	756	21.410
4:12	4:25		103	36	27	23	.58	13	13	75	169	4.786
4:25	5:05	2	104	38	29	29	.67	19	40	115	760	21.523
5:05	6:05	3	105	39	29	24	.79	19	60	175	1140	32.285
6:05	6:35		106	38	29	29	.80	23	30	205	690	19.541
6:35	7:10	4	107	39	29	24	.59	14	35	240	490	13.877
7:10	8:10	5	108	38	29	29	.62	18	60	300	1080	30.586
8:10	9:45		109	39	29	24	.59	14	95	395	1330	37.666
9:45	10:45		110	39	29	29	.62	18	60	455	1080	30.586
10:45	11:10	8	111	39	29	24	.59	14	25	480	350	9.912
11:10	12:25		112	37	28	28	.61	17	75	555	1275	36.108
12:25	1:10	10	113	40	30	26	.51	13	45	600	585	16.567
1:10	2:10	11	114	40	30	29	.53	15	60	660	900	25.488
2:10	3:10	12	115	41	31	28	.52	15	60	720	900	25.488
3:10	5:10	14	116	43	32	30	.53	16	120	840	1920	54.374
5:10	6:45	16	117	41	31	28	.52	15	95	935	1425	40.356
TOTALS		15.6	18	--	--	--	--	--	--	935		

TABLE 3. SUMMARY DATA, NO. 1 TEST, COKE OVEN DOOR LEAKAGE
REPUBLIC STEEL, YOUNGSTOWN, OHIO 4/1-2/76 (Continued)

Clock Time		Approximate Hours Into Test	Filter Number	Particulate Weight on Filter, grams	Particulate Concentration in Leakage Gas, mg/m^3	Particulate Weight for Period,$^{(e)}$ grams	Leakage Flow Through Filter for Period (e) m^3	Particulate Concentration in Leakage Gas for Period,$^{(e)}$ mg/m^3	Particulate Emission Rate, mg/min
On	Off								
3:10	3:21		100	5.9494	1364				
3:21	3:30		101	9.3877	2834				
3:30	4:12	1	102	10.0692	470				
4:12	4:25		103	3.8342	801	25.4063	29.084	874	409.8
4:25	5:05	2	104	5.7531	267				
5:05	6:05	3	105	5.0010	155	9.5873	26.309	364	180.9
6:05	6:35		106	1.9813	101				
6:35	7:10	4	107	5.6064	404				
7:10	8:10	5	108	3.1818	104	12.5887	65.703	192	100.7
8:10	9:45		109	2.7937	74				
9:45	10:45		110	1.3152	43				
10:45	11:10	8	111	0.8054	81				
11:10	12:25		112	1.2681	35	8.0961	108.75	74	33.7
12:25	1:10	10	113	0.6783	41				
1:10	2:10	11	114	0.0528	2				
2:10	3:10	12	115	0.0482	2				
3:10	5:10	14	116	0.0488	1	2.0474	103.651	20	8.5
5:10	6:45	16	117	0.0616	2	0.1104	94.730	1	0.5
TOTALS		15.6				57.8362	428.227	135	61.9

(a) Average flow from Hi-Vol flow chart as recorded during period of flow through filter.

(b) Average gas temperature reading (208 F) and average barometer reading (29.01" Hg) at filter during test used to establish correction factor of 0.77; corrected to 29.92" Hg and 70F.

(c) Odd numbered filters used with No. 1 Hi-Vol and even numbered filters used with No. 2 Hi-Vol; No. 1 Hi-Vol required a calibration correction in the range operated of -16 percent; No. 2 did not require calibration correction in the range at which it operated.

(d) Dilution factor = $\frac{\text{Hi-Vol, cfm + Orifice, cfm - cfm air input under hood}}{\text{Hi-Vol, cfm + Orifice, cfm}}$

(e) Period refers to discrete test periods of 1 hr, 1 hr, 2 hr, 4 hr, 4 hr, and 4 hr.

TABLE 4. NO. 2 TEST, COKE OVEN DOOR LEAKAGE

REPUBLIC STEEL, YOUNGSTOWN, OHIO
4/1-2/76

Clock Time ON	Clock Time OFF	Approximate Hours Into Test	Filter Number	Average Uncorrected Filter Flow As Recorded on Hi-Vol Chart, cfm(a)	Corrected Filter Flow, scfm(b)	Flow Through Filter With Hi-Vol Calibration Correction, scfm(c)	Dilution Correction Factor(d)	Net Leakage Flow Through Hi-Vol, scfm	Time of Flow Through Filter, minutes	Total Time, minutes	Leakage Flow Through Filter, ft^3	Leakage Flow Through Filter, m^3
1303	1304		119	38	29	29	.81	23	1	1	23	0.65
			120	28	22	18	.78	14	1	2	14	0.40
			121	38	29	29	.81	23	4	6	92	2.61
			122	28	22	18	.78	14	3	9	42	1.19
			123	37	28	28	.81	23	16	25	368	10.42
			124	20	15	13	.76	10	9	34	90	2.55
			125	35	27	27	.81	22	3	37	66	1.87
			126	30	23	19	.78	15	3	40	45	1.27
			127	32	25	25	.80	20	3	43	60	1.70
			128	30	23	19	.78	15	5	48	75	2.12
			129	36	28	28	.81	23	4	52	92	2.61
1400	1405	1	130	28	22	18	.78	14	5	57	70	1.98
			131	30	23	23	.79	18	6	63	108	3.06
			132	32	25	21	.79	17	7	70	119	3.37
			133	32	25	25	.80	20	8	78	160	4.53
			134	40	31	26	.80	21	16	94	336	9.52
			135	30	23	23	.79	18	10	104	180	5.10
1456	1506	2	136	32	25	21	.79	17	10	114	170	4.81
			137	30	23	23	.79	18	11	125	198	5.61
			138	35	27	23	.79	18	7	132	126	3.57
			139	30	23	23	.79	18	14	146	252	7.14
			140	28	22	18	.78	14	6	152	84	2.38
			141	32	25	25	.80	20	11	163	220	6.23
1555	1607	3	142	38	29	24	.49	12	12	175	144	4.08
			143	30	23	23	.48	11	12	187	132	3.74
			144	34	26	22	.47	10	11	198	110	3.12
			145	36	28	28	.52	15	12	210	180	5.10
			146	32	25	21	.48	10	12	222	120	3.40
1654	1708	4	147	25	19	19	.45	9	14	236	126	3.57
			148	30	23	19	.45	9	17	253	153	4.33
			149	30	23	23	.48	11	16	269	176	4.98
1741	1755	5	150	34	26	22	.43	9	14	283	126	3.57
1755	1825		151	33	25	25	.46	12	30	313	360	10.20
1825	1912	6	152	36	28	24	.45	11	47	360	517	14.64
1912	1922		153	38	29	29	.45	13	10	370	130	3.68
1922	2000	7	154	37	28	24	.41	10	38	408	380	10.76
2000	2105	8	155	35	27	27	.44	12	65	473	780	22.09
2105	2150	9	156	30	23	19	.37	7	45	518	315	8.92
2150	2225		157	35	27	27	.44	12	35	553	420	11.89
2225	2325	10	158	38	29	24	.41	10	60	613	600	16.99
2325	2351	11	159	30	23	23	.41	9	26	639	234	6.62
2351	0100	12	160	38	29	24	.41	10	69	708	690	19.54
0100	0215	13	161	40	31	31	.47	15	75	783	1125	31.86
TOTALS		13.2	43	--	--	--	--	--		783		

TABLE 4. NO. 2 TEST, COKE OVEN DOOR LEAKAGE

REPUBLIC STEEL, YOUNGSTOWN, OHIO
4/1-2/76 (Continued)

Clock Time		Approximate Hours Into Test	Filter Number	Particulate Weight on Filter, grams	Particulate Concentration, in Leakage Gas, mg/m^3	Particulate Weight for Period,$^{(a)}$ grams	Leakage Flow Through Filter for Period,$^{(a)}$ m^3	Particulate Concentration in Leakage Gas for Period,$^{(a)}$ mg/m^3	Particulate Emission Rate, mg/min
ON	OFF								
1303	1304		119	0.6162	948				
			120	2.3429	5857				
			121	1.5054	577				
			122	7.6181	6402				
			123	9.9949	959				
			124	10.0939	3958				
			125	4.4263	2367				
			126	5.1016	4017				
			127	4.8536	2855				
			128	5.3571	2527				
			129	4.2589	1632				
1400	1405	1	130	4.9861	2518	61.1550	29.37	2082	1002.5
			131	2.4750	809				
			132	5.0502	1499				
			133	7.4640	1648				
			134	7.9094	831				
			135	5.4523	1069				
1456	1506	2	136	5.5386	1151	33.8895	30.39	1115	555.6
			137	5.2461	935				
			138	3.5385	991				
			139	3.5813	502				
			140	3.1257	1313				
			141	3.3512	538				
1555	1607	3	142	3.3360	818	22.1788	29.01	765	363.6
			143	2.9323	784				
			144	2.6086	836				
			145	2.1009	412				
			146	2.2416	659				
1654	1708	4	147	2.2274	624	12.1108	18.93	640	198.5
			148	2.6734	617				
			149	1.9769	397				
1741	1755	5	150	2.1100	591	6.7603	12.88	525	143.8
1755	1825		151	3.1065	305				
1325	1912	6	152	2.2147	151	5.3212	24.84	214	69.1
1912	1922		153	1.0781	293				
1922	2000	7	154	2.8202	262	3.8983	14.44	270	81.2
2000	2105	8	155	3.0858	140	3.0858	22.09	140	47.5
2105	2150	9	156	2.0096	225	2.0096	8.92	225	44.7
2150	2225		157	1.5319	129				
2225	2325	10	158	1.3301	73	2.8620	28.88	99	30.1
2325	2351	11	159	0.5264	80	0.5264	6.62	80	20.2
2351	0100	12	160	0.2584	13	0.2584	19.54	13	3.7
0100	0215	13	161	0.0761	2	0.0761	31.86	2	1.0
TOTALS		13.2	43			154.1322	277.77	555	195.1

Footnotes same as TABLE 3, page 33.

over a period of 935 minutes, collected 57.8 grams of particulate from a calculated gas flow through the filters due to door leakage of 428 cubic meters, and indicates an overall particulate concentration in the door leakage gas of 135 mg/m^3. By comparison, Table 4 shows that Test No. 2 required 43 filters over 783 minutes, collected 154 grams of particulate from total door leakage gas flow through the filters of 278 m^3, and indicates an overall particulate concentration in the door leakage gas of 555 mg/m^3.

Figure 3 is a graphic presentation of particulate concentrations for the door leakage gas plotted against time in hours into the test. Figure 4 shows the emission rate in mg/min, for Test Nos. 1 and 2. For these figures, each curve point is established by data for one sampling segment and is plotted against the time mid-point of that time segment.

It is important to recognize that gas flow values for the Hi-Vol sampler presented in both Tables 3 and 4 are values obtained from the recorder charts on the samplers. Conversely, Hi-Vol flow values shown in Table 1 are instantaneous values recorded during the test.

One important result from Tables 3 and 4 is the fact that the overall particulate concentration for Test 2 was 4.1 times as great as the emission rate measured in Test No. 1. There are a number of possible reasons for this wide difference in particulate emission rate, none of which can be supported by very specific data. The most probable explanation is that the oven door did not fit on as tightly for Test No. 2 as had been the case for Test No. 1. It appeared to members of the research team that the oven door and the door frame did not receive as thorough a cleaning prior to the coking cycle of Test 2 as in the case of Test No. 1. However, there was no comparative measure available for cleaning of deposits from the oven door.

Other factors that might affect door leakage are oven temperature and pressure. No detailed data on these parameters were available for both tests, however, operating personnel reported that 8-mm-H_2O back pressure was maintained on all batteries. In response to a request for temperature and pressure information, the following coke-side flue temperatures were measured at approximately 1500 hours April 1.

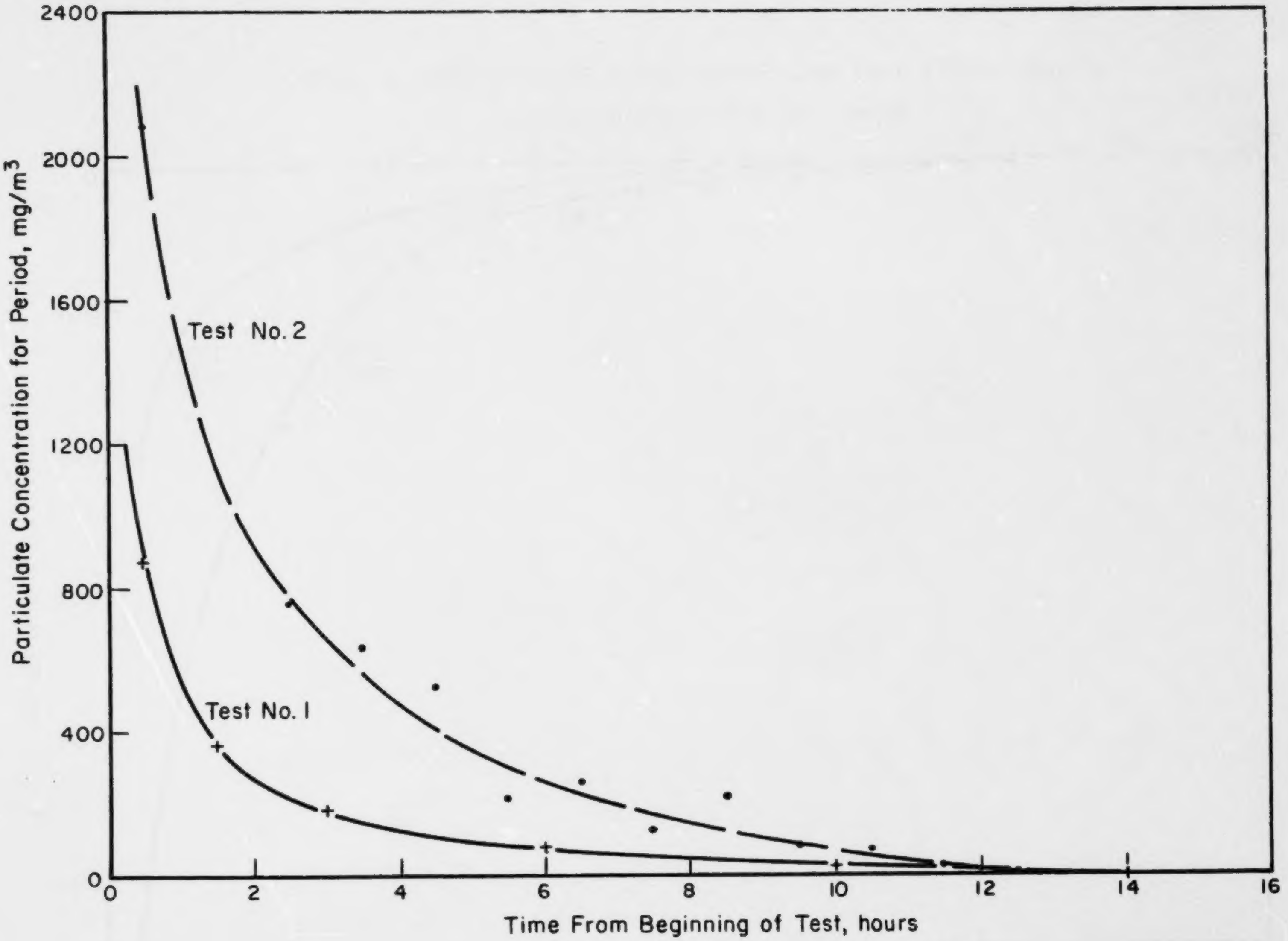

FIGURE 3. PARTICULATE EMISSION CONCENTRATION FOR DOOR-LEAKAGE GAS VS TIME INTO COKING CYCLE

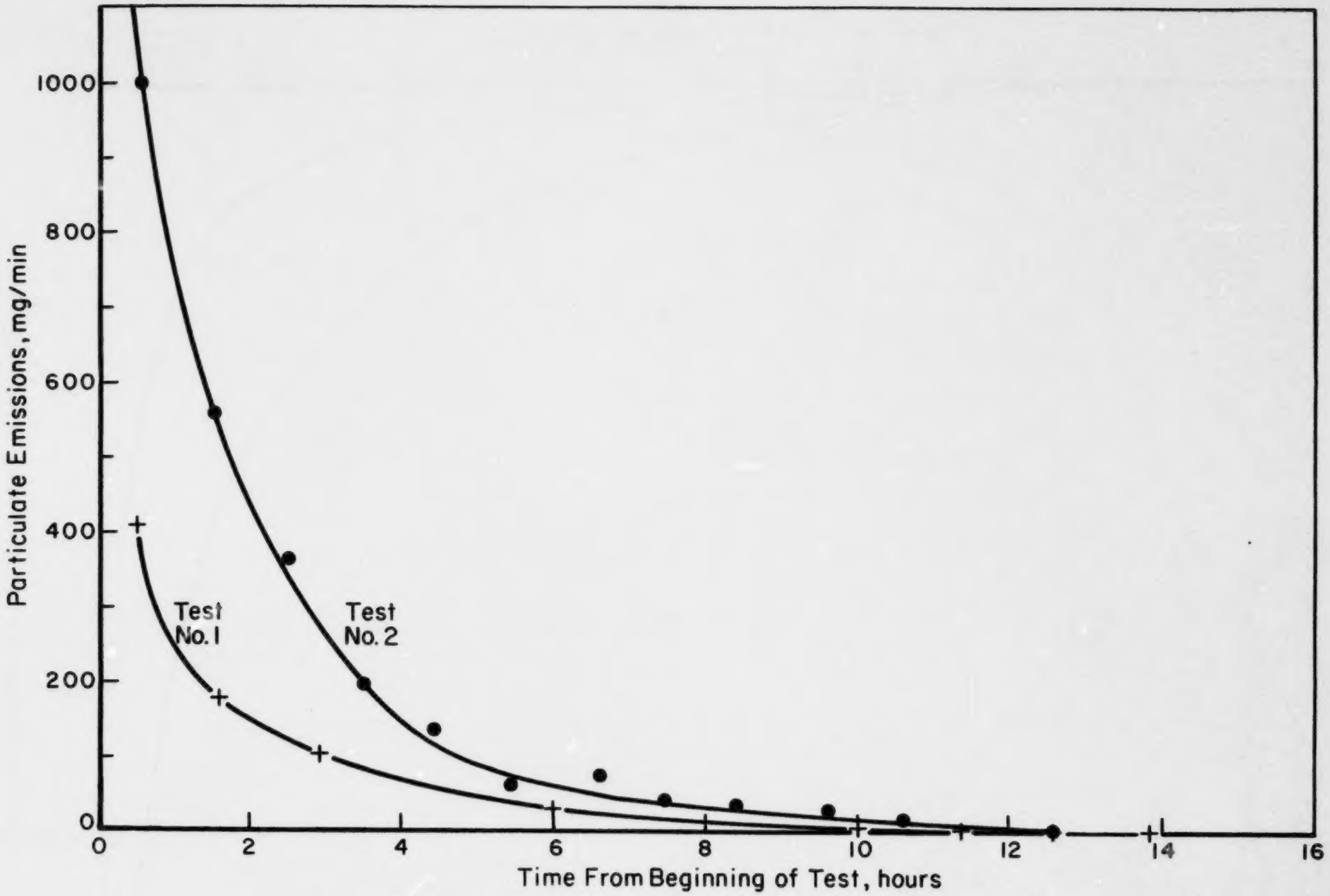

FIGURE 4. PARTICULATE EMISSION VS TIME INTO COKING CYCLE

Flue No.	Temperature, C	F
1	1338	2440
2	1371	2500
3	1382	2520
4	1382	2520
5	1382	2520
6	1371	2500
7	1382	2520
8	1393	2540
9	1382	2520
10	1360	2480
11	1360	2480
12	1349	2460
13	1327	2420

In general, operating personnel reported pusher side flue temperatures to be 1316 C (2400 F) and coke side to be 1371 C (2500 F). They also mentioned that, in the past, normal back pressures had been as high as 14-mm H_2O.

RESULTS OF LEVEL 1 ANALYSES

Gravimetric-Analysis

Table 5 presents results for the gravimetric analysis conducted on the filter and adsorber samples as part of the Level 1 analysis. Results are presented in mass units per hour. Each filter weight was corrected for the total amount of material that would have been obtained if the entire sample extract had been analyzed.

Infrared Spectroscopy

The interpretation of the infrared spectra (and subtracted spectra) of the 88 samples (8 fractions of 11 samples) are summarized in Tables 6 and 7. For several of the fractions, the spectra indicated only the presence of inorganic Si-O components. From past samples we have demonstrated that these inorganic components arise from background components and not from the collected sample. Thus, the samples where only inorganic material has been observed have been marked insufficient sample. From the method of preparing the sample for infrared analysis and from the method of running the spectra, this means that less than 100 nanograms of organic material was present.

An example of the FT-IR technique and the subtractive procedure is the identification of carbozole in Fraction 3 of several of the samples; this is

TABLE 5. LEVEL 1 ANALYSES, GRAVIMETRIC RESULTS

Fraction	1	2	3	4	5	6	7	8
Filter					g/hr			
A1F	8.28	22.71	7.93	6.62	2.88	.87	10.09	.50
A2F	2.79	20.36	4.95	3.75	3.74	.96	9.25	.61
A3F	1.52	11.70	3.44	2.60	1.40	1.68	3.94	.74
A4F	.88	4.99	1.33	1.20	.88	.58	1.39	.10
A5F	.31	.15	.33	.26	.23	.08	.30	.01
Adsorber					mg/hr			
A1	1966.40	2704.20	159.29	335.43	497.72	103.42	321.35	5.08
A2	3275.03	1429.73	213.51	613.83	571.13	143.35	293.83	7.37
A3	1000.43	1097.24	81.54	189.34	127.58	106.22	96.69	2.60
A4	1202.53	879.45	10.43	137.74	271.89	27.09	75.91	3.66
A5	581.42	1067.07	44.56	106.57	231.11	17.17	64.89	2.89
A6(a)	20.98	3.26	1.01	.96	1.10	.91	6.37	.18

(a) Compressor Air Blank.

TABLE 6. LEVEL 1 IR ANALYSIS OF LC FILTER FRACTIONS

Fraction Sample	1	2	3	4	5	6	7	8
A1F	Aliphatic Hydrocarbons Fused Ring Aromatics (a)		Possible Carbazole	* Phenol (c) C≡N (d)	Phenol or Amine (b) (b) *		Aromatic Carboxylic Acid (b)	Insufficient Sample
A2F	Aliphatic Hydrocarbons Fused Ring Aromatics		C≡N (d) Carbazole	Phenol			Aromatic Carboxylic Acid	Insufficient Sample
A3F	Aliphatic Hydrocarbons Fused Ring Aromatics *		C≡N (d) Phenol (b) Carbazole		Aromatic Carboxylic Acid		*	Insufficient Sample
A4F	Aliphatic Hydrocarbons Fused Ring Aromatics		* C≡N (d) Carbazole (c)	Phenol (b)	Aromatic Carboxylic Acid			Insufficient Sample
A5F	Aliphatic Hydrocarbons * Fused Ring Aromatics (a)		C≡N (d) Ketone	Phenol	Ester Phthalate	Aromatic Carboxylic Acid *		Insufficient Sample

(a) Possibly contains pyrene and/or benzpyrenes. * Sample subjected to GC-MS analysis.
(b) Possibly S compounds.
(c) Possibly carbazole types.
(d) Possibly C≡N or (less likely) C≡C.

TABLE 7. LEVEL 1 IR ANALYSIS OF LC ADSORBER FRACTIONS

Fraction Sample	1	2	3	4	5	6	7	8
A1	Aliphatic Hydrocarbons	Fused Ring Aromatics (a)	Nitrile(c)(d) Carbazole(b)	Conjugated Ketone* * Non-conj. Ketone A Phenols	Non-conj. Ketone B			Insufficient Sample
A2	Aliphatic Hydrocarbons Naphthalene *	Fused Ring Aromatics(a)	Carbazole(b) Nitrile(c)	Conj. Ketone(d) Non-conj. Ketone A Phenols	Non-conj. Ketone B	*		Insufficient Sample
A3	Aliphatic Hydrocarbons Naphthalene	Fused Ring Aromatics(a)	Carbazole(c) *	Conj. Ketone(d) Non-conj. Ketone A Phenols	Non-conj. Ketone B		*	Insufficient Sample
A4	Aliphatic Hydrocarbons Naphthalene	Fused Ring Aromatics(a)	Insufficient Sample	Conj. Ketone(d) Non-conj. Ketone A Phenols	Non-conj. Ketone B			Insufficient Sample
A5	Aliphatic Hydrocarbons Naphthalene	* Fused Ring Aromatics(a)	Carbazole	Phenols(d) Conj. Ketone(d) Non-conj. Ketone A	Non-conj. Ketone B	Phthalate ester	*	Insufficient Sample
A6	Aliphatic Hydrocarbons	* Silicons	Trace Aromatics *	Trace Aromatics	Insufficient Sample		Non-conj. Ketone * — Phthalate	Insufficient Sample

Footnotes for Table 7.

(a) Pyrenes and benzpyrenes are likely in this fraction.
(b) Probably primarily carbazole.
(c) Nitrile is most likley but the possibility of $C\equiv C$ cannot be excluded in dramatic p subs nitrile is most likely.
(d) Can be conjugated ketone, quinone or mixture of both.

* Sample subjected to GC-MS analysis.

illustrated in Figure 5. The top spectrum is an absorbance spectrum of Fraction 4 of Sample A1F; the bottom spectrum is an absorbance spectrum of Fraction 3 of Sample A1F. The two spectra in the middle of Figure 4 are the resultant of subtracting the spectrum of Fraction 3 from two different ratios of Fraction 4. These two subtracted spectra show:

(1) Carbazole is the main component of Fraction 3

(2) Similar components in both Fraction 3 and Fraction 4

(3) Correct intensities of Fraction 4 by removing the contribution (carbazole) of Fraction 3, thus aiding in the identification of Fraction 4.

Another example of the subtraction technique is given in Figure 6. At the top of this figure is an absorbance spectrum of Fraction 6 of Sample A2. At the bottom is a spectrum of Fraction 3 of this same sample. Note that these spectra show many similarities making it difficult (because the separation might not be clean) to identify the unique components of each fraction. In the middle of Figure 6 is the resultant of subtracting the spectrum of Fraction 5 from that of Fraction 6. The absorption pointing up and down near 1700 cm^{-1} clearly determines that:

(1) Fractions 5 and 6 have different (but very similar) carbonly absorptions

(2) The positions (frequencies) of each carbonyl vibration coupled with the other observed bands in each fraction identifies both as non-conjugated ketones, and each fraction as having a different ketone structure. These ketones were designated as Ketone A and Ketone B.

GAS CHROMATGRAPHY-MASS SPECTROSCOPY RESULTS

The major species determined by the GC-MS analysis of selected samples are listed in Table 8. Examples of EI and CI reconstructed gas chromatograms, with the more abundant species labeled, are shown in Appendix C. Individual mass spectra for the CI GC-MS analysis are also given in Appendix C.

Results obtained by the semiquantitation procedure for identified GC-MS components are listed in Table 9.

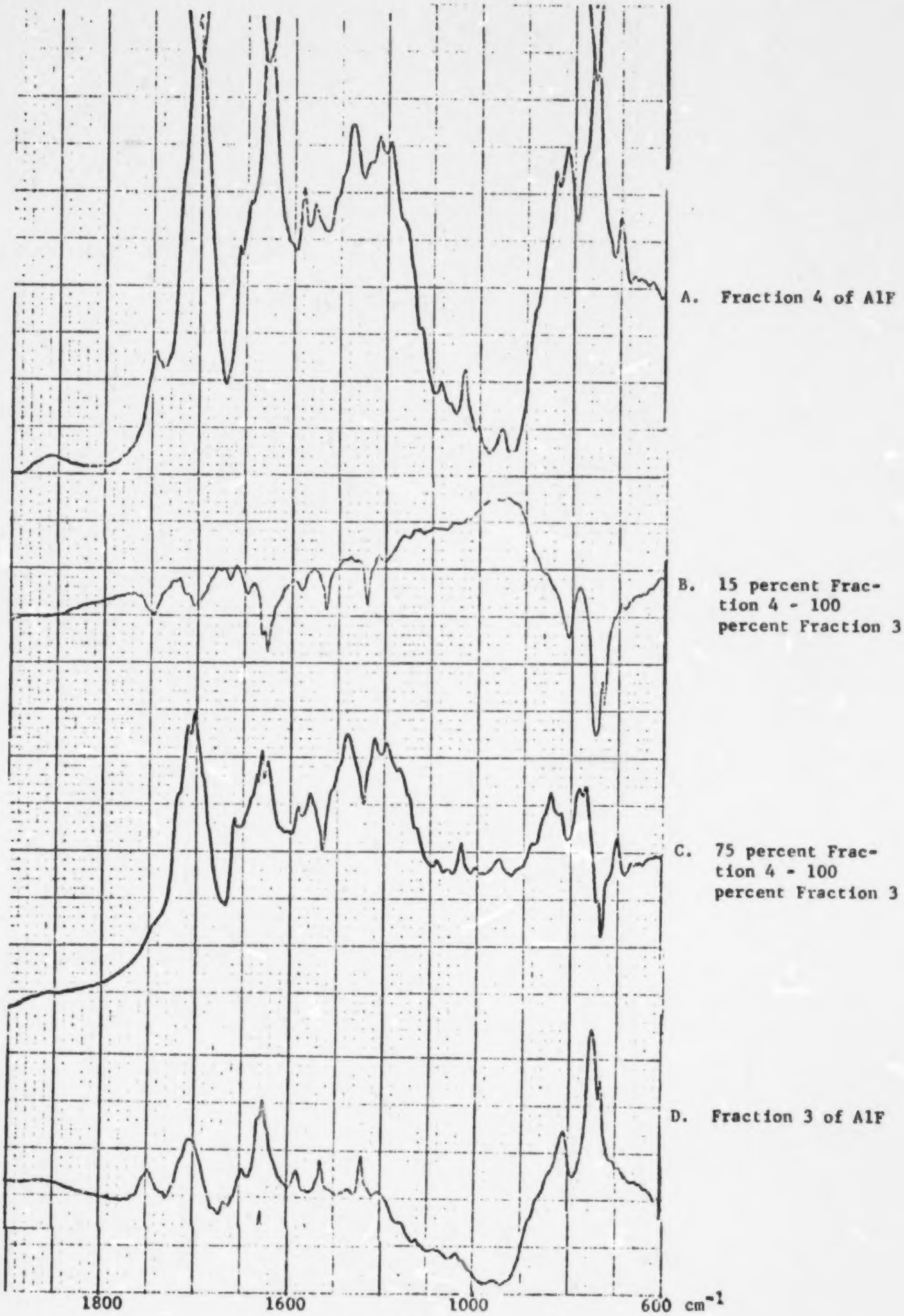

FIGURE 5. ABSORBANCE INFRARED SPECTRA

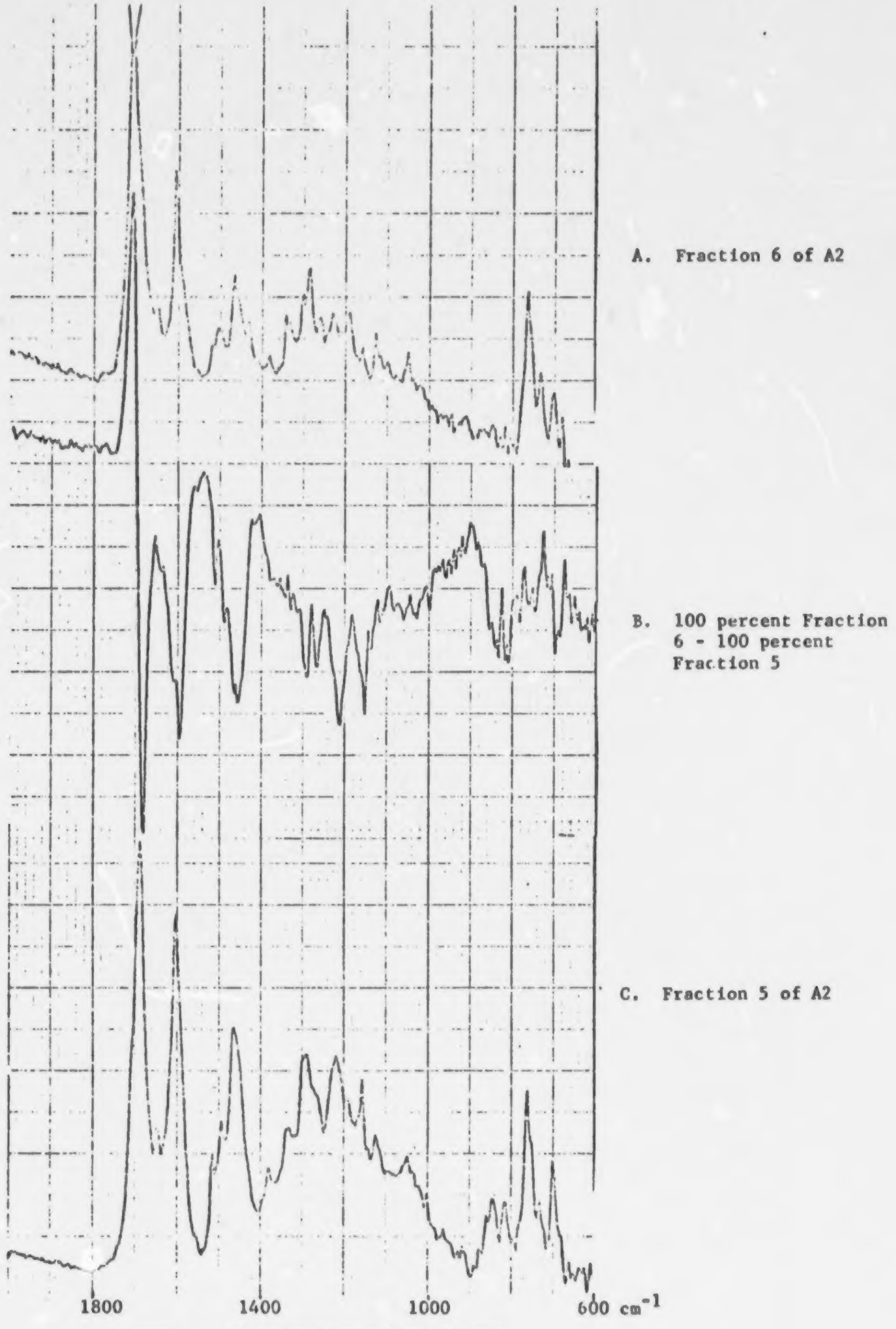

FIGURE 6. ABSORBANCE INFRARED SPECTRA

TABLE 8. GC-MS ANALYSES OF SELECTED COKE OVEN DOOR SAMPLE FRACTIONS

Fraction	Sample	Compounds Identified[(a)]
		Adsorbent Samplers
1	A2	Naphthalene, methylnaphthalenes, dihydronaphthalene, C_2-naphthalene
2	A5	Naphthalene, methylnaphthalenes, anthracene, acenaphthalene, methyl acenaphthalene/ fluorene, biphenyl acenaphthene/ methyl biphenyl, tetrahydronaphthalene, indene
3	A1	Indole, naphthylisocyanide, carbazole methyl carbazole
3	A5	Carbazole, methyl carbazole
4	A1	C_2-phenol
5	A1	C_2-phenol, C_3-phenol
6	A2	No positive identification
7	A5	Quinoline, phthalate, acridine
7	A3	No positive identification
8	A11	No GC components
		Filters
1	A3F	Anthracene, methylanthracene, fluorene, methylfluorene, fluoranthene, methylfluoranthene, pyrene, methylpyrene, phthalate
2	A5F	Anthracene, methylanthracene, fluoranthene, methylfluoranthene, pyrene, methylpyrene, benzphenanthrene, chrysene, benzopyrene, benzofluoranthene, methyl chrysene/ methyl benznathracene, methyl benzopyrene/ methyl benzfluoranthene, coronene
3	A3F	Carbazole, methylcarbazole, benzanthrone, cyanofluorene, dimethyl carbazole

TABLE 8. GC-MS ANALYSES OF SELECTED COKE OVEN DOOR SAMPLE FRACTIONS (Continued)

Fraction	Sample	Compounds Identified[a]
4	A1F	(2)C_3-phenol, C_2-benzaldehyde, naphthol, methylnaphthol, hydroxyfluorene, methoxyfluorene, benzanthrone
5	A1F	C_3-phenol
6	A5F	No identification
		Filters
7	A4F	Quinoline, phthalate
8	A1F	No GC components
		Compressor Air Supply (Blank)
2	A6	No positive identification
3	A6	Naphthalene, anthracene
7	A6	Phthalate

(a) See text.

TABLE 9. SEMIQUANTITATION OF SELECTED COKE OVEN DOOR SAMPLE FRACTIONS

Fraction	Sample	Compound	Percent of Total Emission	Emission Rate, mg/hr
1	A3F	Fluorene	2	30
		Methyl fluorenes	2	30
		Anthracene	21	320
		Methyl anthracenes	12	180
		Pyrene	10	150
		Methyl pyrenes	10	150
		Fluoranthene	12	180
		Phthalate	5	75
2	A5F	Anthracene	5	7.5
		Fluoranthene	15	22
		Pyrene	10	15
		Methyl pyrenes/methyl fluoranthenes	4	6.0
		Dimethyl pyrenes/dimethyl fluoranthenes	1	1.5
		Benzo phenanthrenes	4	6.0
		Chrysene	21	31
		Methyl chrysenes/benzoanthracenes	4	6.0
		Dibenzo anthracenes	2	3.0
		Benzo fluoranthenes	15	22
		Benzo pyrenes	11	16
		Methylbenzopyrenes/methylbenzo-fluoranthenes	1	1.5
		Indeno pyrene	4	6.0
		Benzo perylene	4	6.0
		Coronene	1	1.5
3	A3F	Carbazole	29	95
		Methyl carbazoles	13	43
		Dimethyl carbazoles	6	20
		Cyanofluoranthene	5	16
		Benzanthrone	3	10
		Phthalate	3	10
4	A1F	C_2 benzaldehydes	6	400
		C_3 phenol	7	460
		Methyl allyl phenol	3	200
		Methyl indenone	5	330
		Naphthol	7	460
		Methyl naphthols	14	920
		Hydroxy fluorene	7	460
		Methoxy fluorene	1	65
		Benzanthrone	6	400

TABLE 9. SEMIQUANTITATION OF SELECTED COKE OVEN DOOR SAMPLE FRACTIONS (Continued)

Fraction	Sample	Compound	Percent of Total Emission	Emission Rate, mg/hr
7	A4F	Quinoline	19	265
		Phthalate	16	220
1	A2	Naphthalene	35	1100
		Methyl naphthalenes	26	850
		Dimethyl naphthalenes	8	260
		Dihydroxy naphthalene	5	160
2	A5	Indene	10	100
		Naphthalene	33	350
		Methyl naphthalene	19	200
		Tetrahydro naphthalene	3	30
		Acenaphthalene	11	120
		Biphenyl/acenaphthrene	6	60
		Methyl biphenyl/methyl acenaphthrene/fluorene	6	60
		Anthracene	3	30
		Methyl anthracene	1	10
		Dimethyl anthracenes	0.05	0.5
		Trimethyl anthracenes	0.05	0.5
		Fluoranthene	1	10
		Pyrene	1	10
		Methyl pyrenes/methyl fluoranthenes	0.1	1.0
		Benzophenanthrene	0.05	0.5
		Chrysene	0.07	0.7
3	A1	Indole	19	30
		Methyl indole	6	9.0
		Carbazole	25	40
		Methyl carbazole	3	5.0
		Naphthyl isocyanide	25	40
3	A5	Carbazole	57	25
		Methyl carbazole	16	7.0
		Phthalate	16	7.0
4	A1	C_2 phenol	53	180
		Alkyl phenol	20	68
5	A1	C_2 phenol	11	55
		C_3 phenol	8	40

TABLE 9. SEMIQUANTITATION OF SELECTED COKE OVEN DOOR SAMPLE FRACTIONS (Continued)

Fraction	Sample	Compound	Percent of Total Emission	Emission Rate, mg/hr
7	A5	Quinoline	15	10
		Methyl quinolines	3	2.0
		Dimethyl quinolines	5	3.0
		Acridine	7	4.5
		Methyl acridines	4	2.5
		Benz acridines	1	0.6
		3 Phenyl propanilide	10	6.5
		Methyl 3 phenyl propanilide	6	4.0
		Phthalate	53	34

THIN LAYER CHROMATOGRAPHY RESULTS

Results of the quantitation of BaP as determined by TLC are listed in Table 10. This quantitation was performed only on the filters extracted by EPA with cyclohexane.

HIGH RESOLUTION MASS SPECTROMETRY RESULTS

The results of the HRMS analyses conducted by Dr. Sharkey are listed in Tables 11, 12, and 13. The nine formulas, listed in Table 13, include highly carcinogenic PNA's. Few of these possible structures were found in the extracts of the absorber column, while there were strong indications for all except 3-methyl-cholanthrene (mass 268) in the filter extracts.

TRACE METAL RESULTS

Results of trace metals emissions, as determined by the SSMS analysis described earlier, are presented in Table 14. Each element is reported in μg above the blank for the entire sample collected.

Differences among samples in detection limits of a given element arise from differences in items such as degree of plate fogging and/or plate sensitivity and sometimes differences in sample composition. In these analyses, differences are related to plate characteristics. Also, detection limits for many of the elements are mandated by the elemental blank levels of the glass fiber. This is especially true for the alkali and alkaline earth elements as well as for some of the transition elements such as Zn and Zr.

SSMS results for analyses of the coal and coke samples are presented in Table 15.

GASEOUS EMISSIONS

The light hydrocarbons and inorganic components detected in the flask samples for Test No. 1 and 2 are presented in Table 16 and 17, respectively. These results are calculated on a dry basis; the amount of water detected is shown at the bottom of each table. Water was much higher for Test No. 2 results which might be due to the fact it rained during this test.

For compounds present at concentrations lower than the sensitivity of the analysis technique, values are reported as less than 0.1 ppm or less than 50 ppm of the component was present. In the first instance a more sensitive

TABLE 10. TLC QUANTITATION RESULTS FOR BaP

Sample	μg	mg/hr
A1F	710	5.0
A2F	440	4.0
A3F	700	2.7
A4F	540	1.1
A5F	230	.35

TABLE 11. LOW VOLTAGE MASS SPECTROMETRIC RESULTS OBTAINED ON FIBER SAMPLES

Major Structural Type, Including Alkyl Derivatives	Total Ionization, percent(a) AIF	A2F	A3F	A4F	A5F
ϕ-Naphthalenes	8.8	8.5	9.6	9.2	8.2
6-Ring Peri	.3	1.7	.4	.9	1.9
3-Rings	16.5	10.0	12.4	7.4	4.2
1,12-Benzoperylenes	1.3	4.0	2.0	3.2	4.8
Benzonaphthothiophenes	2.0$^{b/}$	2.2$^{b/}$	2.3	2.3	2.2
5-Ring Cata	1.6	3.9	2.2	3.2	3.1
Acenaphtyhlenes + Fluorenes	8.6	5.4	4.5	2.9	4.5
5-Ring Peri	8.3	15.1	11.6	13.4	16.0
Dibenzothiophenes	3.5$^{c/}$	2.2$^{c/}$	2.5	1.9	1.6
ϕ-3-Rings or Binaphthyls	3.5	4.9	4.2	5.1	4.5
4-Ring Cata	10.7	12.1	13.4	20.8	18.1
4-Ring Peri	17.9	17.8	23.7	19.4	21.4
Coronenes	.2	.5	-	.2	.5
Dinaphthothiophenes	-	-	.6	-	-

(a) Percent total ionization assumes equal sensitivity for all components. Valid for comparison of similar samples.
(b) Confirmed by HRMS.
(c) Not confirmed by HRMS.

Note: 3-Ring compounds are anthracene and phenathrene
4-Ring peri compounds are pyrene and fluoranthene
4-Ring cata compounds are chrysene, 3.4-benzphenanthrene, tetraphene, and tetracene
5-Ring peri compounds are perylene, benzo(a)pyrene, benzo(e)pyrene
5-Ring cata compounds includes 11 5-ring compounds
6-Ring peri compounds includes 11 6-ring compounds

TABLE 12. LOW VOLTAGE MASS SPECTROMETRIC RESULTS OBTAINED ON ADSORBER SAMPLES

	Total Ionization, percent[(a)]					
	A1	A2	A3	A4	A5	A6
Benzenes	3.4	4.6	11.7	4.2	4.5	-
Indanola/Benzothiophenes	2.4	1.6	1.7	2.8	3.1	-
ϕ-Naphthalenes	.9	.3	.4	.5	.6	-
Phenols	9.9	19.5	17.6	18.1	16.4	-
3-Rings	6.3	4.1	2.6	3.0	4.0	-
Acenaphthylenes + Fluorenes	8.5	5.3	3.6	5.4	6.1	-
5-Ring Cata	.1	-	-	-	-	-
Acenaphthenes + Biphenyls	4.3	3.9	2.6	4.0	4.4	-
Dibenzofurans	3.2	-	-	-	-	-
Naphthalenes	42.1	42.2	39.5	44.7	47.0	-
Dibenzothiophenes	1.0	.5	.2	.2	.3	-
Indenes	7.0	6.9	11.6	8.3	7.4	-
4-Ring Cata	.6	-	-	.2	.2	-
Indans/Tetralins	3.2	1.8	2.8	2.2	2.1	-
Benzofurans	2.7	2.0	3.7	2.7	1.1	-
4-Ring Peri	1.7	1.0	.9	1.6	1.7	-
5-Ring Peri	-	-	-	-	.1	-

(a) Percent total ionization assumes equal sensitivity for all components. Valid for comparison of similar samples.

Note: See note on Table 11.

TABLE 13. HIGH RESOLUTION MASS SPECTROMETRIC RESULTS

		Sample Identification						Sample Identification				
m/e	Formula	A1	A2	A3	A4	A5	A6	A1F	A2F	A3F	A4F	A5F
228	$C_{18}H_{12}$	△ ●	▲ ○	△ ●	△ ●	▲ ●	△ ○	▲ ●	▲ ○	▲ ●	▲ ○	▲ ○
252	$C_{20}H_{12}$	△ ●	▲ ○	▲ ○	△ ○	▲ ○	△ ○	▲ ●	▲ ○	▲ ●	▲ ○	▲ ○
254	$C_{20}H_{14}$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	▲ ●	▲ ○	△ ●	▲ ○	△ ○
256	$C_{20}H_{16}$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	▲ ●	▲ ○	▲ ●	▲ ○	△ ○
267	$C_{20}H_{13}N$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	▲ ○ □	▲ ○ ■	▲ ○ ■	▲ ○ ■	▲ ○ ■
268	$C_{21}H_{16}$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○
278	$C_{22}H_{14}$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	▲ ●	▲ ○	▲ ●	▲ ○	▲ ○
279	$C_{21}H_{13}N$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	▲ ○ □	▲ ○ □	▲ ○ ■	▲ ○ ■	▲ ○ □
302	$C_{24}H_{14}$	△ ○	△ ○	△ ○	△ ○	△ ○	△ ○	▲ ○	▲ ○	▲ ○	▲ ○	▲ ○

● - Detected by HRMS (photoplate)

○ - Not detected by HRMS (photoplate)

■ - Detected by HRMS peak matching

□ - Not detected by HRMS peak matching

▲ - Detected by HRMS (computer run) data system

△ - Not detected by HRMS (computer run) data system

TABLE 14. SSMS ANALYSIS OF FILTER SAMPLES

Element	A1F	A2F	A3F	A4F	A5F	A1F	A2F	A3F	A4F	A5F
	μg					μg/g				
Li	1.5	10	0.5	<0.002	<0.01	0.024	0.32	0.015	<0.00010	<0.0017
Be	<10	<10	<10	<10	<2,000	<0.16	<0.32	<0.29	<0.52	<350
F	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Na	<150,000	<150,000	<150,000	<150,000	<150,000	<2400	<4800	<4400	<7900	<26,000
Mg	<5,000	<5,000	<5,000	<5,000	<5,000	<79	<160	<150	<260	<870
Al	<7,000	<7,000	<7,000	<7,000	<7,000	<110	<220	<204	<370	<1,200
P	<50	<50	<50	<50	<50	<0.79	<1.6	<1.5	<2.6	<8.7
S	<10,000	<10,000	<10,000	<10,000	<10,000	<160	<320	<290	<520	<1,700
K	<20,000	<20,000	<20,000	<20,000	<20,000	<310	<640	<580	<1000	<3,500
Ca	<30,000	<30,000	<30,000	<30,000	<30,000	<470	<950	<870	<1600	<5,200
Sc	<20	<20	<20	<20	<20	<0.31	<0.64	<0.58	<1.0	<3.5
Ti	50	<50	<50	<50	<50	0.79	<1.6	<1.5	<2.6	<8.7
V	<10	<10	<10	<10	<10	<0.16	<0.32	<0.29	<0.52	<1.7
Cr	100	50	10	<10	10	1.6	1.6	0.29	<0.52	1.7
Mn	10	<10	<10	<10	<10	0.16	<0.32	<0.29	<0.52	<1.7
Fe	1,000	500	1,000	500	300	16	16	29	26	<52
Co	10	<10	<10	<10	<10	0.16	<0.32	<0.29	<0.52	<1.7
Ni	50	30	<30	<30	<30	0.79	0.95	<0.87	<1.6	<5.2
Cu	30	10	50	10	20	0.47	0.32	1.5	0.52	3.5
Zn	≤100	≤100	≤100	≤100	≤100	≤1.6	≤3.2	≤2.9	≤5.2	≤17
Ga	<10	<10	<10	<10	<10	<0.16	<0.32	<0.29	<0.52	<1.7
Ge	≤20	≤20	≤20	≤20	≤20	≤0.31	≤0.64	≤0.58	≤1.0	≤3.5
As	30	<20	<20	<20	<20	0.47	<0.64	<0.58	<1.0	<3.5
Se	<10	<10	<10	<10	<10	<0.15	<0.32	<0.29	<0.52	<1.7
Br	30	10	≤10	<10	<10	1.3	0.32	≤0.29	<0.52	<1.7
Rb	30	≤30	≤30	≤30	≤30	0.47	≤0.95	≤0.87	≤1.6	≤5.2
Sr	≤30	≤30	≤30	≤30	≤30	≤0.47	≤0.95	≤0.87	≤1.6	≤5.2
Y	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Zr	<20	<20	<20	<20	<20	0.31	<0.64	<0.58	<1.0	<3.5
Nb	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Mo	10	<10	<10	<10	<10	0.16	<0.32	<0.29	<0.52	<1.7
Ru	<5	<5	<5	<5	<5	<0.079	<0.16	<0.15	<0.26	<0.87
Rh	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.1	<0.35
Pd	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.1	<0.35
Ag	10	<5	<5	<5	<5	0.16	<0.16	<0.15	<0.26	<0.87
Cd	<5	<5	<5	<5	<5	<0.079	<0.16	<0.15	<0.26	<0.87

TABLE 14. SSMS ANALYSIS OF FILTER SAMPLES (Continued)

Element	A1F	A2F	A3F	A4F	A5F	A1F	A2F	A3F	A4F	A5F
			μg					μg/g		
In	<5	<5	<5	<5	<5	<0.079	<0.16	<0.15	<0.26	<0.87
Sn	500	<20	<20	<20	<20	7.9	<0.64	<0.58	<1.0	<3.5
Sb	≤10	<10	<10	<10	<10	≤0.16	<0.32	<0.29	<0.52	<1.7
Te	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
I	0.5	<0.5	<0.5	<0.5	<0.5	<0.0079	<0.016	<0.015	<0.026	<0.087
Cs	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Ba	<500	<500	<500	<500	<500	<7.9	<16	<15	<26	<87
La	50	<1	<1	<1	<1	0.79	<0.032	<0.029	<0.052	<0.17
Ce	100	<1	<1	<1	<1	1.6	<0.032	<0.029	<0.052	<0.17
Pr	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Nd	<3	<3	<3	<3	<3	<0.047	<0.095	<0.087	<0.16	<0.52
Sm	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Eu	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Gd	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Tb	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Dy	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Ho	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Er	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Tm	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Yb	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Lu	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
Hf	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Ta	<2	<2	<2	<2	<2	<0.031	<0.064	<0.058	<0.10	<0.35
W	1	<1	<1	<1	<1	0.016	<0.032	<0.029	<0.052	<0.17
Re	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Os	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Ir	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Pt	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Au	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Hg	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Tl	<1	<1	<1	<1	<1	<0.016	<0.032	<0.029	<0.052	<0.17
Pb	1,000	<100	<100	<100	<100	16	<32	<29	<52	<17
Bi	15	5	<0.5	<0.5	<0.5	0.24	0.16	<0.015	<0.026	<0.087
Th	<0.5	<0.5	<0.5	<0.5	<0.5	<0.0079	<0.016	<0.015	<0.026	<0.087
U	<0.5	<0.5	<0.5	<0.5	<0.5	<0.0079	<0.016	<0.015	<0.026	<0.087
B	<2,000	<2,000	<2,000	<2,000	<2,000	<31	<64	<58	<100	<35

TABLE 15. MASS SPECTROGRAPHIC ANALYSES OF COAL & COKE$^{(b)}$

		Sample Designation			
Element	Coal	Coke	Element	Coal	Coke
Li	30	10 ppm	Sb	<0.5	2 ppm
Be	5	3	Te	<1	3
B	100	100	I	<1	5
F	5	5	Cs	1	20
Na	3000	3000	Ba	100	1000
Mg	5000	2000	La	10	300
Al	~5%	~3%	Ce	20	200
Si	~10%	~10%	Pr	1	100
P	300	300	Nd	10	200
S	3000	5000	Sm	3	10
Cl	100	200	Eu	<1	3
K	500	2000	Gd	1	10
Ca	2000	~2%	Tb	<1	1
Sc	30	30	Dy	3	10
Ti	5000	3000	Ho	<0.5	1
V	100	50	Er	<1	5
Cr	100	20	Tm	<1	<1
Mn	300	300	Yb	<1	5
Fe	~5%	~1%	Lu	<2	0.5
Co	20	20	Hf	<3	<1
Ni	20	100	Ta	<2	<2
Cu	30	30	W	<1	<2
Zn	30	50	Re	<1	<1
Ga	30	20	Os	<2	<5
Ge	2	20	Ir	<3	<3
As	10	20	Pt	<5	<5
Se(a)	≤5	≤20	Au	<2	<2
Br	10	20	Hg	<5	<5
Rb	5	10	Tl	<2	<2
Sr	2000	3000	Pb	1	10
Y	100	100	Bi	<1	<1
Zr	200	200	Th	≤3	5
Nb	2	10	U	≤1	3
Mo	10	20			
Ru	<2	<5			
Rh	<1	<1			
Pd(a)	<1	≤10			
Ag	0.5	5			
Cd	10	10			
In(a)	<0.5	<2			
Sn	1	100			

(a) Memory from previous sample.
(b) Total weight of sample analyzed 100 mg.

TABLE 16. OVEN NO. 41 "A" GAS PHASE, TEST NO. 1

Sample No. & (Hrs^a)	Results Reported as Volume Percent & Volume ppm, Dry Bases											
	1 (0.5)		2 (1.5)		3 (3)		4 (6)		5 (10)		6 (13)	
Component	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Nitrogen	77.40		77.8		79.4		78.0		78.0		78.0	
Oxygen	20.60		20.9		19.4		20.8		20.9		20.9	
Argon	.95		.95		.99		.96		.96		.95	
Carbon dioxide	.09		.08		.06		.05		.05		.05	
Carbon monoxide	.10		.03		.004		.02		.01		.005	
Hvdrogen	.44		.16		<.1		.08		.04		.03	
Methane		3200		900		60		400		100		31
Acetylene & ethene		200		50		3		200		2		.6
Ethane		200		30		2		9		2		.4
Propene		50		9		.3		.4		.2		*
Propane		20		3		.1		.2		.1		*
1-Butene		8		1		*		*		*		*
Iso-Butane		2		*		*		*		*		*
n-Butane		6		.5		*		*		*		*
Benzene		100		**		**		**		**		**
Toluene		62		**		**		**		**		**
Total low MW hydrocarbons		3848		993.5		65.4		609.6		104.3		32
Water	<.1		.2		.2		.6		.3		.2	

a. Number of hours into the run is shown in parenthesis.
* Less than 0.1 ppm.
** Less the 50 ppm.

TABLE 17. OVEN NO. 41 "A" GAS PHASE, TEST NO. 2

Sample No. & (Hrs[a])	Results Reported as Volume Percent & Volume ppm, Dry Bases											
	1 (0.5)		2 (1.5)		3 (3)		4 (6)		5 (10)		6 (13)	
Component	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Nitrogen	76.3		82.9		81.7		80.4		80.5		79.3	
Oxygen	20.5		15.9		16.9		18.3		18.2		19.5	
Argon	.95		1.03		1.00		.98		.99		1.0	
Carbon dioxide	.24		.13		.16		.17		.17		.07	
Carbon monoxide	.16		.003		.03		.02		.02			<0.3
Hydrogen	.81		<.1		.07		.11		.07		<.1	
Methane	.69			<2		30	.04		.04		.01	
Acetylene & ethene	.16			*		60		9		40		0.1
Ethane	.08			*		50		20		7		*
Propene	.02			*		60		2		0.3		*
Propane		84		*		30		0.8		0.3		*
1-Butene		67		*		0.3		0.4		*		*
Iso-Butane		12		*		*		*		0.4		*
n-Butane		32		*		*		*		0.7		*
Pentene		7		**		**		**		**		**
Pentane		16		**		**		**		**		**
Hexane		3		**		**		**		**		**
Benzene		3		**		**		**		**		**
Toluene		*		**		**		**		**		**
Carbonyl sulfide		10		**		**		**		**		**
Carbon disulfide		1		**		**		**		**		**
Total Low MW hydrocarbons		9724		<2		230		432.2		448.7		.1
Water	3.8		0.5		4.6		2.2		0.5		0.4	

a. Number of hours into the run is shown in parenthesis.
* Less than 0.1 ppm.
** Less than 50 ppm.

analytical technique was used; the technique used for those components reported as less than 50 ppm is not capable of detecing a specific quantity less than 50 ppm. Sample No. 1 of Test No. 2 was concentrated which made it possible to detect much lower concentrations of C_5 to C_7 hydrocarbon and other inorganic gases, but few additional compounds were detected.

The gas analysis results support the contention that much greater leakage occurred around the oven door in Test No. 2 compared to Test No. 1. The data for analysis of gaseous grab samples reported in Tables 16 and 17, showed generally higher hydrocarbon contents for Test No. 2 samples compared to Test No. 1 samples. The inorganic products of combustion (carbon dioxide, carbon monoxide, and hydrogen) showed approximately twice the amount for Test No. 2. During Test No. 2, the oxygen content of the gas dropped as low as 15.9 volume percent (Sample 2) and gradually increased to 19.5 percent by the end of the run. This low oxygen content (20.9 percent in normal air) was evident in spite of air addition of about 68 m^3/hr (40 cfm). This is in contrast with Test No. 1 which showed a lower oxygen content of 19.4 percent for Sample 3 with Samples 2, 4, 5, and 6 having an oxygen content close to normal air. In all cases of low oxygen (except Sample 1) for Test No. 2, the inert components of the air (nitrogen and argon) increased above normal which indicates products formed from the oxygen consumption were high molecular weight compounds, or the filter coated with tars and/or the adsorber were removing more of the volatile components before they reached the flask sample.

During the running of Test No. 1, the total light hydrocarbon content decreased with time (as expected since the volatile components should be driven off earlier in the run). Sample 3 was the only exception in this trend. During Test No. 2, Sample 2 showed no hydrocarbons despite the high oxygen consumption and Sample 6 showed less than Sample 4 and 5. It would appear that some of the hydrocarbons were removed from these samples before reaching the flasks, probably by adsorption on a caked filter or in the adsorption bulb.

A partial list of compounds that could be detected by the gas analysis techniques used but not found in the coke oven samples are listed below. The lower limit of detection for these compounds for the concentrated sample (Sample 1, Test 2) is 0.1 ppm, and 50 ppm for the other samples.

Sulfur dioxide
Hydrogen sulfide
Hydrogen chloride
Methyl chloride
Hydrogen cyanide
Nitrogen oxides
C_1 to C_3 alcohols
Acetone

Quantifying Gaseous Emissions

The quantifying of gaseous emissions cannot be done precisely for the coke oven samples. The reason that such quantitation cannot be done is apparent disagreement between gas flow data and the results of the gas analyses.

For example, field test data for Test No. 1 show that the air flow into the hood (as measured at the rotameter) ranged from 15 to 35 scfm, and was mostly between 27 and 35 scfm. Flows out of the hood were 41 to 47 scfm at the orifice and 27 to 30 scfm at the Hi-Vol filter. By addition, the total flow out was about 68 to 77 scfm. Subtracting the air flow into the hood, 27 to 35 scfm, would leave estimated leakage values of 33 to 50 scfm. Thus, the leakage is calculated to be 100 to 150 percent of the inlet air flow.

However, examining the gas analyses, the high values for oxygen and nitrogen (averaging 20.6 and 78.1, respectively) suggests that the flask samples consisted of mostly air. This suggests that the leakage rate through the oven door may have been much lower than the rate of air flow into the hood via the compressor and any leakage at the hood seals.

The best estimate that can be made of gaseous emissions can be made by assuming that the total gas flow out (via the orifice and the Hi-Vol sampler) was measured fairly accurately. Then, by using the flow rate and the gas analysis data, estimates of gaseous emissions can be made. This has been done and is reported in Table 18[*].

RESULTS OF BACTERIAL MUTAGENESIS ANALYSIS

Table 19 shows the results of the average of two experiments with the testor strains on samples A1F, A3F, and A5F. In these assays, the number of

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[*] Because the gas flow rate data was not taken simultaneously with the gas samples, average gas flow rates for the entire test were used to calculate gaseous emissions.

TABLE 18. GASEOUS EMISSION ESTIMATES

Test No.	1						2					
Total Estimated Gas Flow Out, scfm	73.0						72.2					
Total Estimated Gas Flow Out, Nm^3/min	2.06						2.04					
Sample Number	1	2	3	4	5	6	1	2	3	4	5	6
Emission, mg/min												
Carbon monoxide	2,392	717	96	478	239	120	3,790	71	711	474	474	<1
Methane	4,382	1,233	82	548	137	42	9,361	<3	41	543	543	136
Acetylene	462	115	7	462	5	1	3,659		137	21	91	<1
Ethane	513	77	5	23	5	1	2,033		127	51	18	
Propene	180	32	1	1	1		712		213	7	1	
Propane	75	11	<1	1	<1		313		112	3	1	
1-Butene	38	5					318		1	2		
Iso-Butane	10						59				2	
n-Butane	30	2					157				3	
Benzene	787						20					
Toluene	488											
Pentene							41					
Pentane							98					
Hexane							22					
Carbonyl sulfide							51					
Carbon disulfide							6					

TABLE 19. EPA COKE OVEN SAMPLES(5)

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Average of Two Experiments Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		22	4	10	18	86
	+		19	4	13	17	77
Positive controls	-	0.05	201				234
β-Propiolactone	-	0.01		4	15	32	
2-Anthramine	+	0.01		130	1563	1371	
Coke-oven sample A1F	-	0.01	9	1	9	14	68
	-	0.05	16	2	8	17	65
	-	0.10	19	3	8	17	59
	-	0.50	14	8	9	42	61
	-	1.0	23	8	17	81	71
	-	2.5	31	6	30	96	68
	-	5.0	32	20	35	117	88
	+	0.01	10	4	9	21	92
	+	0.05	28	6	14	26	88
	+	0.10	22	15	17	46	84
	+	0.50	24	45	86	153	120
	+	1.0	16	63	116	243	158
	+	2.5	48	74	144	373	166
	+	5.0	54	135	226	415	228

TABLE 19. EPA COKE-OVEN SAMPLES(5) (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Average of Two Experiments Histidine-Positive Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		22	4	10	18	86
	+		19	4	13	17	77
Positive controls							
β-Propiolactone	-	0.05	201				234
2-Anthramine	-	0.01		4	15	32	
	+	0.01		130	1563	1371	
Coke-oven sample A3F	-	0.01	13	2	6	22	64
	-	0.05	17	3	9	17	68
	-	0.10	20	2	8	24	76
	-	0.50	15	7	13	28	83
	-	1.0	20	6	10	37	81
	-	2.5	22	5	9	27	79
	-	5.0	17	10	17	69	74
	+	0.01	17	1	10	25	95
	+	0.05	17	6	13	27	71
	+	0.10	20	8	9	37	86
	+	0.50	19	32	45	91	117
	+	1.0	19	53	71	159	144
	+	2.5	34	56	135	183	146
	+	5.0	40	94	152	293	156

TABLE 19. EPA COKE-OVEN SAMPLES(5) (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 µl of DMSO)	Average of Two Experiments Histidine-Positive Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		25	6	11	23	98
	+		24	3	10	29	104
Positive controls							
β-Propiolactone	-	0.05	213				263
2-Anthramine	-	0.01		4	15	33	
	+	0.01		199	2029	1924	
Coke-oven sample A5F	-	0.01	22	6	6	14	91
	-	0.05	30	7	5	25	68
	-	0.10	34	5	12	18	71
	-	0.50	27	6	9	19	82
	-	1.0	25	9	17	42	74
	-	2.5	19	7	10	57	60
	-	5.0	17	15	23	115	93
	-	10.0	22	toxic	29	119	71
	+	0.01	13	7	9	18	103
	+	0.05	13	5	7	25	101
	+	0.10	21	10	13	29	78
	+	0.50	17	13	21	44	89
	+	1.0	16	30	34	81	103
	+	2.5	41	33	49	128	116
	+	5.0	15	54	85	226	172
	+	10.0	35	toxic	99	172	127

revertants per plate was increased ten-fold over the negative control in strains TA1537, TA1538, and TA98, and two-fold in strain TA100. Metabolic activation (rat-liver homogenate) increased the number of mutants above that observed without activation. The results suggest that coke oven samples A1F, A3F, and A5F are moderately mutagenic and that a frame-shift mutation occurred since TA1535, which is reverted by base-pair substitution mutagens, was not affected. Mutagenic activity was enhanced when the metabolic activitation system was added to the test. The relative order of mutagenic activity was A1F >A3F >A5F.

Table 20 presents the results of the experiments with S. typhimurium on samples A1, A3, A5, and A6. In the first experiment, 0.1 ml of each sample was removed and dissolved in 0.9 ml of DMSO (50 µl = 5 µl of sample). Dilutions were then made so that each dose was in 50 µl of DMSO. In the second experiment, 0.4 ml of sample was dissolved in 1.6 ml DMSO (50 µl = 10 µl of sample) for samples A5 and A6.

Samples A1, A3, and A5 were weakly mutagenic on strains TA1537, TA1538, TA98, and TA100 when a metabolic activation system was added. In the first experiment, the number of histidine revertants per plate increased 2-4 fold over the control plates. In the second experiment, only strain TA100, with metabolic activation, had a 2-fold increase in revertants. These samples also appear to cause frame shift mutations. Sample A6 was not mutagenic in either of the tests.

RESULTS OF MAMMALIAN CELL CYTOTOXICITY STUDIES

Due to the nature of the filter samples, it was not possible to quantitate the dose or concentration of effluent material the cells were exposed to. Control filters were not available for testing. The edge of the filter did not appear to have been exposed to the coke oven emissions and was found not to be toxic to the alveolar macrophages. The center of the filters A1F, A2F, A3F, A4F, and A5F all caused a significant reduction in cellular viability.

In each case, between 5-30 mg of filter was utilized in the cytotoxicity test. It was not possible to quantitate the cytotoxic response or compare relative toxicity of these samples since the emissions were not evenly distributed on the filters and the amount of emissions present in the test was not known.

TABLE 20. EPA COKE-OVEN SAMPLES

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		22	7	15	29	107
	+		19	3	6	34	128
Positive controls							
β-Propiolactone	-	0.05	329				360
2-Anthramine	-	0.01			16	29	
	+	0.01		201	1625	1705	
Coke-oven sample A1	-	0.01	28	8	9	23	82
	-	0.05	19	8	10	16	92
	-	0.10	31	3	17	16	80
	-	0.50	16	6	11	12	88
	-	1.0	23	14	15	15	58
	-	5.0	24	5	8	9	115
	+	0.01	11	5	12	23	77
	+	0.05	7	13	12	26	81
	+	0.10	14	8	9	39	105
	+	0.50	15	7	14	33	82
	+	1.0	14	9	20	28	95
	+	5.0	12	47	68	124	162

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Experiment 2							
Negative control	-		14	9	9	17	110
	+		13	8	14	22	118
Positive controls							
AF-2	-	0.005	408	694	1915	1007	624
2-Anthramine	-	0.01	20	21	17	28	139
	+	0.01	387	543	876	697	880
Coke-oven sample A1	-	0.1	19	6	16	13	115
	-	0.5	22	3	12	9	102
	-	1.0	11	1	7	10	105
	-	2.5	8	5	4	9	91
	-	5.0	8	5	11	12	115
	-	10.0	7	6	6	1	100
	+	0.1	12	15	20	13	150
	+	0.5	16	12	18	27	154
	+	1.0	10	6	32	19	155
	+	2.5	10	10	26	12	159
	+	5.0	12	20	18	17	253
	+	10.0	7	18	20	toxic	245

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 µl of DMSO)	Histidine-Positive Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		22	7	15	29	107
	+		19	3	6	34	128
Positive controls							
β-Propiolactone	-	0.05	329				360
2-Anthramine	-	0.01			16	29	
	+	0.01		201	1625	1705	
Coke-oven sample A3	-	0.01	29	1	8	19	83
	-	0.05	29	2	9	15	84
	-	0.10	31	6	15	19	79
	-	0.50	24	6	12	20	89
	-	1.0	25	5	6	12	72
	-	5.0	16	5	9	18	67
	+	0.01	5	7	10	29	84
	+	0.05	10	5	12	26	82
	+	0.10	16	5	13	27	85
	+	0.50	10	10	14	34	90
	+	1.0	7	7	16	33	74
	+	5.0	15	10	28	62	116

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 µl of DMSO)	Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Experiment 2							
Negative control	-		14	9	9	17	110
	+		13	8	14	22	118
Positive control							
AF-2	-	0.005	408	694	1915	1007	624
2-Anthramine	-	0.01	20	21	17	28	139
	+	0.01	387	543	876	697	880
Coke-oven sample A3	-	0.1	27	11	6	9	131
	-	0.5	18	9	7	20	110
	-	1.0	20	5	4	23	98
	-	2.5	12	4	5	18	126
	-	5.0	11	9	3	17	85
	-	10.0	7	6	10	12	91
	+	0.1	15	11	19	29	122
	+	0.5	13	10	14	21	128
	+	1.0	8	5	26	27	177
	+	2.5	7	13	21	38	164
	+	5.0	10	12	26	53	198
	+	10.0	15	77	35	40	211

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Histidine-Positive Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		22	7	15	29	107
	+		19	3	6	34	128
Positive controls							
β-Propiolactone	-	0.05	329				360
2-Anthramine	-	0.01			17	29	
	+	0.01		201	1625	1705	
Coke-oven sample A5	-	0.01	14	2	18	23	77
	-	0.05	17	5	11	19	78
	-	0.10	23	5	9	16	88
	-	0.50	27	6	7	27	82
	-	1.0	19	6	10	13	75
	-	5.0	14	toxic	4	14	68
	+	.01	14	4	12	17	86
	+	.05	5	5	18	24	80
	+	.10	10	6	15	27	88
	+	.50	7	11	18	25	62
	+	1.0	18	5	22	31	94
	+	5.0	7	18	40	73	123

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 µl of DMSO)	Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Experiment 2							
Negative control	-		14	9	9	17	110
	+		13	8	14	22	118
Positive controls							
AF-2	-	0.005	408	694	1915	1007	624
2-Anthramine	-	0.01	20	21	17	28	139
	+	0.01	387	543	876	697	880
Coke-oven sample A5	-	0.1	19	16	17	30	161
	-	0.5	24	6	14	11	142
	-	1.0	15	11	11	10	139
	-	2.5	14	5	13	toxic	96
	-	5.0	toxic	toxic	toxic		toxic
	-	10.0					
	+	0.1	7	13	14	15	131
	+	0.5	17	11	18	14	191
	+	1.0	23	11	25	29	210
	+	2.5	14	7	19	toxic	193
	+	5.0	9	4	18		107
	+	10.0	toxic	toxic	toxic		toxic

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Negative control	-		19	5	12	22	137
	+		20	8	20	31	104
Positive controls							
β-Propiolactone	-	0.05	280	375			315
2-Anthramine	-	0.01			14	32	
	+	0.01			1545	1661	
Coke-oven sample A6	-	0.01	22	5	3	22	108
	-	0.05	15	5	8	28	77
	-	0.10	22	6	10	30	102
	-	0.50	14	3	10	20	73
	-	1.0	9	4	10	18	86
	-	5.0	16	2	9	6	62
	+	0.01	15	8	7	27	98
	+	0.05	6	4	9	16	105
	+	0.10	15	5	6	28	81
	+	0.50	20	7	16	30	126
	+	1.0	9	4	3	24	90
	+	5.0	14	12	13	22	100

TABLE 20. EPA COKE-OVEN SAMPLES (Continued)

Compound	Metabolic Activation	Microliters of Sample (in 50 μl of DMSO)	Histidine-Positive Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
Experiment 2							
Negative control	-		27	5	7	17	88
			28	3	15	24	80
Positive control							
β-Propiolactone	-	0.05	97				166
2-Anthramine	-	0.01		4	14	36	
		0.01		196	2432	2143	
Coke-oven sample A6	-	0.10	20	2	7	26	74
	-	0.50	17	3	7	16	60
	-	1.0	15	4	4	18	64
	-	2.5	14	3	7	12	60
	-	5.0	17	2	5	16	58
	-	10.0	18	2	13	9	40
	+	0.10	29	4	9	31	59
	+	0.50	27	2	8	17	53
	+	1.0	31	4	5	22	60
	+	2.5	15	2	7	15	63
	+	5.0	28	4	16	27	67
	+	10.0	26	8	6	20	64

DISCUSSION OF RESULTS

As would be expected during devolatilization of organic materials, such as coal, the rate at which materials are emitted is high initially and then decreases with time. Figure 4 and Table 5 shows that this phenomena was observed at the coke plant - particulate emissions were greater than 1000 mg/min during the first hour and decreased to less than 1 mg/min near the end of the coking cycle. Thus, even though filters and adsorbent columns were changed more frequently during the early part of the test, the filters and adsorbent columns used during the early part of the coking cycle were much more heavily loaded than those used later in the cycle.

The large variation is mass emission between the two tests raises questions concerning using results of a small number of runs to determine emission factors or emission estimates for these sources.

Highly complex sample mixtures such as coke oven effluents are extremely difficult to analyze qualitatively, even more so quantitatively. The Level-1 analytical strategy followed here has enabled a semi-quantitative determination of the predominate classes of organic components present in the samples obtained.

Infrared analysis of the Level-1 fractions failed to detect any significant differences in the composition of the emissions during the coking cycle. However, the LC fractions obtained in the Level-1 analysis remain highly complex and, therefore, not easily amenable to detailed infrared analysis.

GC-MS analyses were conducted on representative fractions, as determined by infrared analysis; these analyses also proved difficult due to the highly complex nature of the fractions yielding insufficient GC resolution. In many cases, the mass spectral data obtained for these unresolved GC components proved too complex for adequate interpretation. Nevertheless, the predominate classes of organic components that were identified by infrared analysis were subsequently identified by GC-MS.

HRMS further confirmed the presence of many components identified by GC-MS. In addition, HRMS detected dibenzothiophenes and a $C_{21}H_{13}N$ component which were not observed using GC-MS.

Bioassay results for the total sample are of limited value, since infrared and GC-MS confirmed the presence of a large number of known hazardous species such as polynuclear aromatic hydrocarbons present in these samples. Since many of such compounds are mutagenic and/or cytotoxic, we would clearly expect the positive bioassay results obtained in this study.

RECOMMENDATIONS

Further studies which involve the chemical analysis and bioassay of coke emissions should include provisions for obtaining higher resolution fractionation of the samples. This would include HPLC size and class separation which would yield fractions which were more amenable to successful infrared and mass spectral analyses.

Bioassay tests should be conducted after the LC or, preferably, HPLC fractionation. They would then give an indication as to which fractions merit further analysis, giving a more complete overview of such coke oven emissions.

REFERENCES

1. B. Commoner. Chemical Carcinogens in the Environment. Chapter 4 in Identification and Analysis of Organic Pollutants in Water. Ed. by L. H. Keith, Ann Arbor Science Publ., Ann Arbor, MI, 1976.

2. Jones, P. W., Graffeo, A. P., Detrick, R., Clarke, P. A., and Jakobsen, R. J. Technical Manual for Analysis of Organic Materials in Process Streams. EPA-600/2-76-072. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., March, 1976.

3. Kier, L. D., Yamasaki, E., and Ames, B. N. Detection of Mutagenic Activity in Cigarette Smoke Condensate. Proc. Nat. Acad. Sci. USA. 71:4159-4163, 1974.

4. Ames, B. N., McCann, J. and Yamasaki. Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mammalian-Microsome Mutagenicity Test. Mut. Res., 31:347-364, 1975.

5. Simmon, V. F., Poole, D. In Vitro Microbiological Mutagenicity, Studies of Seven Coke-Oven Samples. Stanford Research Institute Report No. LSU-3493. Submitted to EPA, Research Triangle Park, NC, January 6, 1977.

6. Waters, M. D., et al. Environmental Research, 9:32-47, 1975.

APPENDIX A

THERMAL ANALYSIS OF COKE OVEN DOORS

SUMMARY REPORT

on

THERMAL ANALYSIS OF COKE OVEN DOORS
(Contract No. 68-02-1409, Task 16)

to

U.S. ENVIRONMENTAL PROTECTION AGENCY

June 12, 1975

by

G. R. Whitacre, S. E. Miller, and J. B. Purdy

BATTELLE
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SUMMARY REPORT

on

THERMAL ANALYSIS OF COKE-OVEN DOORS

to

U.S. ENVIRONMENTAL PROTECTION AGENCY

from

BATTELLE
Columbus Laboratories

by

G. R. Whitacre, S. E. Miller, and J. B. Purdy

June 6, 1975

INTRODUCTION

As part of a study of concepts for minimizing emissions from coke-oven doors (Contract No. 68-02-1439), a system was developed at Battelle for measuring the emissions escaping from oven doors. Figure 1 shows the hood used to capture emissions from around the oven door. In its original form, the hood had a natural aluminum shiny surface on both inside and outside, and the outside surface was covered with a 1-inch thickness of glass fiber backed on its outside surface with aluminum foil. The system was tested on a Koppers oven at Empire-Detroit Steel in Portsmouth, Ohio. The system performed satisfactorily. However, with the hood installed on the oven buckstays, and natural convection over the oven door cut off, the surface temperature of the door rose about 65 C (150 F) above a similar spot temperature on a nearby door. The comparison door was charged 10 to 15 minutes later than the test door.

The temperature rise caused by installation of the hood was undesirable for two reasons: (1) uncontrolled temperature rise might cause damage to an oven door, and (2) excessive temperature above normal could result in abnormal samples of emissions collected for analysis through expansion of leakage cracks or through thermal change of leakage products.

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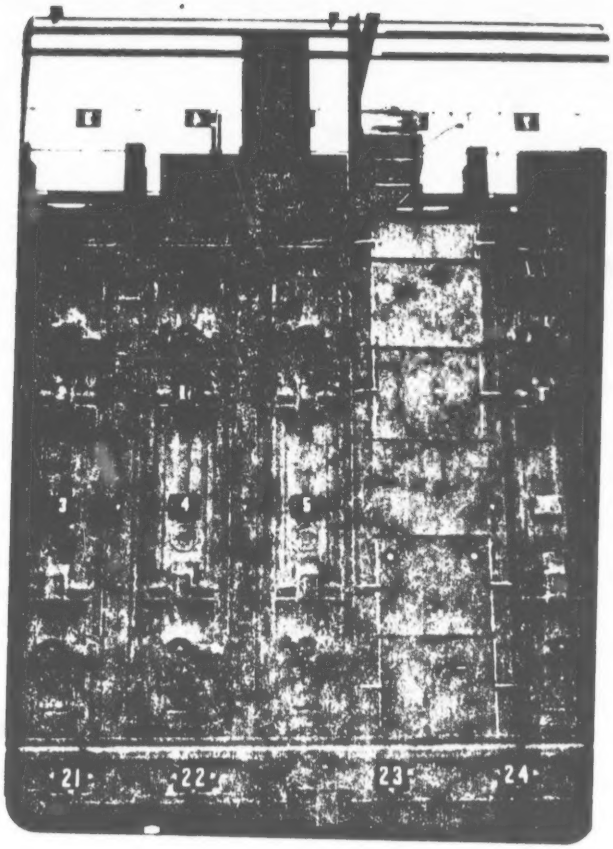

FIGURE 1. SAMPLING HOOD INSTALLED ON
COKE OVEN

It was proposed that certain control steps be taken to control temperature rise, and that normal door temperature levels be established by a test run over a complete normal coking cycle. Proposed control steps were:

(1) Remove glass fiber insulation from the hood

(2) Increase the amount of purge air released beneath the hood

(3) Blacken both sides of the hood to increase heat radiation

(4) Remove hood for a cooling-off period when oven door temperatures rise to a predetermined point.

In order to determine the effectiveness of the proposed modifications for control of door temperature, EPA authorized Task 16. This task provided for measurement of door temperatures throughout a normal coking cycle. It also authorized a heat-transfer analysis to provide the following information:

(1) Quantification of heat flux, under normal operating conditions, identifying the proportion of heat loss due to convection and radiation

(2) On a theoretical basis, determine what the increase in door temperature would be with the testing hood installed in the original test condition. Compare these calculations to conditions actually observed.

(3) Theoretically determine the temperature effect that darkening the inside of the shield and removing the insulation will have without increasing the purge-gas flow rate.

(4) Show the temperature effect, including the above modifications, of increasing the purge-gas flow rate throughout the range of 30 cfm to 90 cfm. A graph of gas flow rate versus total heat dissipation is expected.

(5) On a theoretical basis, show the temperature effect of intermittent removal of the hood indicating approximate rate of door temperature decrease after removal.

A meeting to review this work was held on June 3 with Mesrs. Richard Rovang and Norman Plaks of EPA. Two suggestions were made by Mr. Plaks that might further improve heat transfer and reduce door temperatures when the sampling hood is in place. Thus, a sampling run might be made over an entire coking cycle with door temperatures remaining close to those of a normal coking cycle. The suggestions were:

(1) Install small fins (about 1/4 inch high) in a vertical position on the inside and possibly on the outside of the hood sections to aid in heat transfer

(2) Provide air circulation in back of the hood by use of several fans or blowers.

It was agreed that a brief study of these approaches would be made prior to any extensive sampling program, to determine the degree of improvement they may provide and to help in design and placement of the fins. Also, it was agreed that this brief investigation should be made a preliminary part of any sampling program.

SUMMARY AND CONCLUSIONS

Door temperatures were measured by eight thermocouples throughout one 15-hour coking cycle. Figure 2 is a schematic illustration of the door size and the relative locations of the thermocouples.

The No. 7 thermocouple, 267 cm (105 inches) from the bottom of the door, registered the highest peak and average temperatures. The peak temperature recorded was about 213 C (416 F) and the average temperature value for No. 7 thermocouple was 206 C (403 F).

Following one complete coking cycle with recorded temperatures, the sampling hood was installed for a period of 2 hours and 20 minutes. As shown by Figure 1, the insulation had been removed from the hood and its surfaces were painted black. Purge air was fed under the hood at a rate of 1.7 m^3/min (60 ft^3/min). Temperature on No. 7 thermocouple rose from 204 C (400 F) to 241 C (465 F), an increase rate of 0.26 C/min (0.46

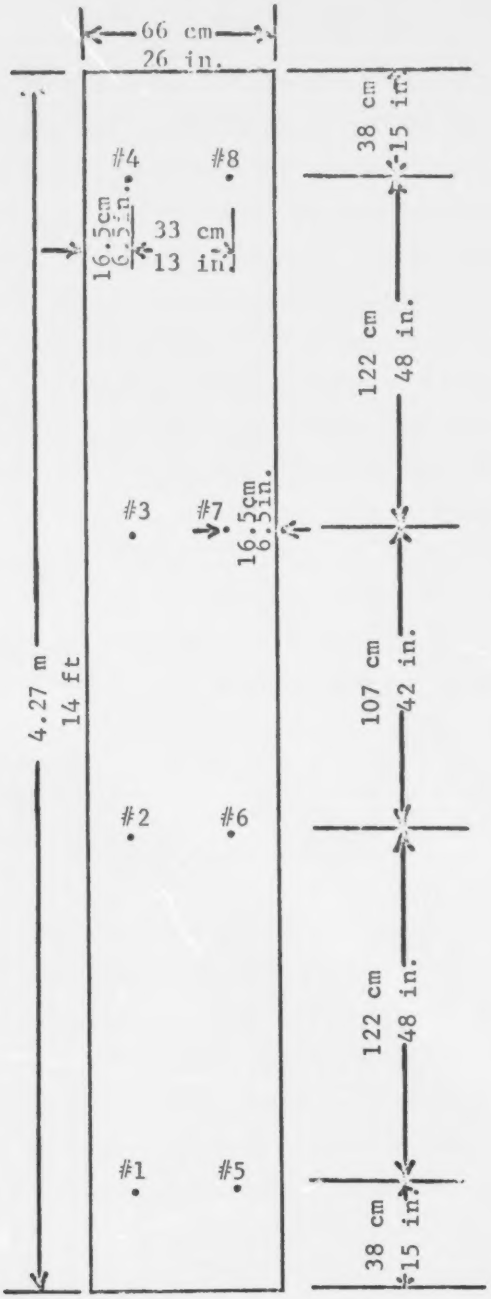
66 cm
26 in.
#4
#8
16.5cm
6.5in.
33 cm
13 in.
#3
#7
16.5cm
6.5in.
#2
#6
#1
#5
4.27 m
14 ft
38 cm
15 in.
122 cm
48 in.
107 cm
42 in.
122 cm
48 in.
38 cm
15 in.

FIGURE 2. THERMOCOUPLE LOCATIONS, NO. 6
COKE-OVEN DOOR

F/min). The hood was then removed and in 1 hour the temperature had decreased to 221 C (430 F), a rate of decrease of 0.67 C/min (0.58 F/min).

From temperatures recorded during the test run on the coke oven door, a theoretical heat analysis was made. It consisted of heat loss due to convection and radiation, door temperatures with various hood emissivities and purge air flows, and the door temperatures with insulation on the hood.

Table 1 summarizes the temperatures and heat flux calculated under conditions of 0.85, 1.70, and 2.5 m^3/min (30, 60, and 90 ft^3/min) air flow in combination with emissivities (ϵ) of 0.9 and 0.2 on both sides of the hood. Calculations were also made for an air flow of 1.7 m^3/min (60 ft^3/min) with emissivities of 0.9 and 0.2 applied to the inside and outside surfaces of the hood respectively, and then 0.2 and 0.9 applied to the inside and outside surfaces, respectively.

The door temperature calculated with 1.7 m^3/min purge air flow and with both sides of the hood painted black (ϵ = 0.9) was 248 C (478 F); this temperature as measured during the test run after 2 hours and 20 minutes was 241 C (465 F). At 241 C the hood was removed with the temperature still slightly on the rise. Therefore, the calculated door temperature of 248 C (478 F) appears to be reasonable.

Calculations show that the total heat dissipated by convection levels off at about 2.5 m^3/min (90 ft^3/min) of purge air. Calculated door temperature with insulation on the outside surface was 399 C (750 F). Over the purge air range of 0.85-2.5 m^3/min (30-90 ft^3/min), calculated door temperatures vary from 343 C (650 F) to about 306 C (582 F) with shiny aluminum surface on both sides of the hood; by painting only the outside surface black, door temperature is lowered only about 1.7 C (3 F). Painting the inside surface black and leaving the outside shiny drops the door temperature 54 C (97 F), and painting both inside and outside surfaces black lowers door temperature 66 C (119 F).

Hood temperature is less affected than door temperature by emissivity change due to painting both hood surfaces black. At a purge-air flow of 0.85 m^3/min (30 ft^3/min), hood temperature is 141 C (286 F)

TABLE 1. SUMMARY OF RESULTS OF HEAT TRANSFER ANALYSIS

Air Flow, m^3/min and ft^3/min	ϵ_{in}	ϵ_{out}	T_{door}, Degrees, C and F	T_{air}, Degrees, C and F	T_{hood}, Degrees, C and F	$T_{insulation}$ Outside Surface Degrees, C and F	Heat Flux {w/m^2 and Btu/ft^2hr: q to purge air	q to ambient air	Total q
0.85	0.9	0.9	261.0	101.8	127.0		1078.7	1687.3	2766.3
30			502.0	215.2	260.5		341.9	534.8	876.8
1.7	0.9	0.9	248.0	69.1	134.1		1389.1	1422.0	2808.6
60			478.0	156.5	237.3		440.3	450.7	890.2
2.5	0.9	0.9	239.6	54.2	106.2		1556.0	1276.5	2834.4
90			463.3	129.5	223.1		493.2	404.6	898.4
0.85	0.2	0.2	343.1	128.0	141.4		1394.2	1111.2	2505.4
30			649.5	263.0	286.5		441.9	352.2	794.1
1.7	0.2	0.2	314.0	85.4			1770.9	826.6	2598.1
60			597.0	185.8	242.0		561.3	262.0	823.5
2.5	0.2	0.2	306.0	64.0			1902.8	722.8	2624.6
90			582.0	148.0	222.0		603.1	229.1	831.9
1.7	0.9	0.2	260.0	77.0	148.1		1574.3	1191.6	2769.8
60			500.0	170.5	298.5		499.0	377.7	877.9
1.7	0.2	0.9	201.0	79.0	89.7		1632.1	969.8	2603.5
60			594.0	175.0	193.5		517.3	307.4	825.2
With Insulation on Hood:									
0.85	0.2	0.2	393.0	172.5	284.2	75.3	1917.3	425.3	2345.4
30			740.0	342.5	543.5	167.5	607.7	134.8	743.4

NOTES: ϵ = emissivity factor; T = temperature, C and F; q = heat flux, w/m^2 and Btu/ft^2hr.

Cubic feet x 0.0283 = cubic meters; Heat flux, Btu/ft^2hr x 3.155 = w/m^2 .

versus 127 C (260 F) when both sides of the hood are painted. As purge air flow is increased, hood temperature under the two emissivity conditions becomes more nearly equal and at 2.5 m^3/min (90 ft^3/min) it is equal under the two purge-air flow conditions.

The tests and theoretical analyses show that removal of hood insulation and increased emissivity from painting both sides of the hood black are effective in lowering door temperature. Although normal door temperature is not maintained by these steps alone, theoretical analysis shows that at 1.7 m^3/min purge-air flow door temperature should be about 248 C (478 F). The actual test run of over 2 hours made on April 25 verifies this calculated temperature; a maximum temperature of 240 C (464 F) was recorded with indications that the temperature was starting to stabilize. A run of 3 hours' duration under these test conditions could undoubtedly be completed, and the test just completed shows that hood removal results in a rapid lowering of door temperature. The increase in door temperature of 36 to 42 C (65 to 75 F) that would probably result from the type of test run just completed, would not, in the opinion of Battelle chemistry analytical authorities, have a harmful effect on samples obtained. Metallurgical experts advise that this much temperature rise in this temperature range will not be harmful to the oven door.

It is possible that further improved heat dissipation such as from fins on the hood may enable a run to be made over a complete cycle without removing the hood.

DISCUSSION OF THE PROGRAM

Test Setup

Eight thermocouples, numbered and located as shown in Figure 2, were installed on the door of No. 6 coke oven at the Koppers battery of Empire-Detroit, Portsmouth, Ohio. Figures 3, 4, and 5 show details of

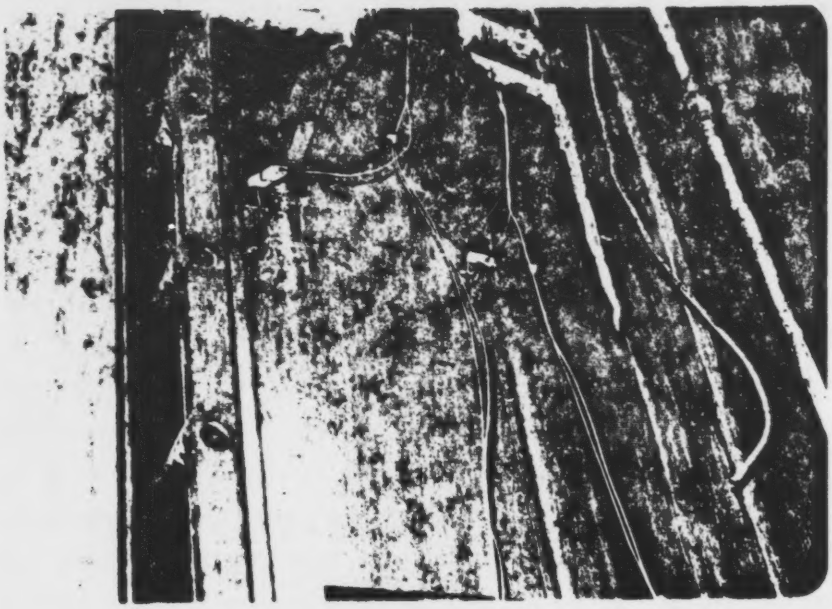

FIGURE 3. CLOSEUP OF THERMOCOUPLES NO. 4 AND 8 SHOWING LEADS TO RECORDER, AND SECTION OF PURGE AIR PIPE (UPPER RIGHT CORNER)

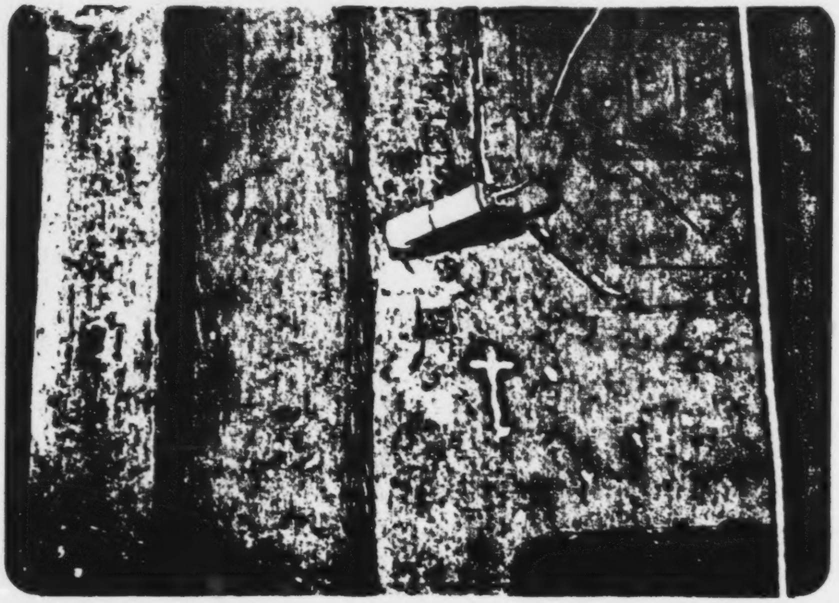

FIGURE 4. CLOSEUP OF THERMOCOUPLE NO. 2 SHOWING DETAIL OF QUICK DISCONNECT PLUG IN THERMOCOUPLE LEAD

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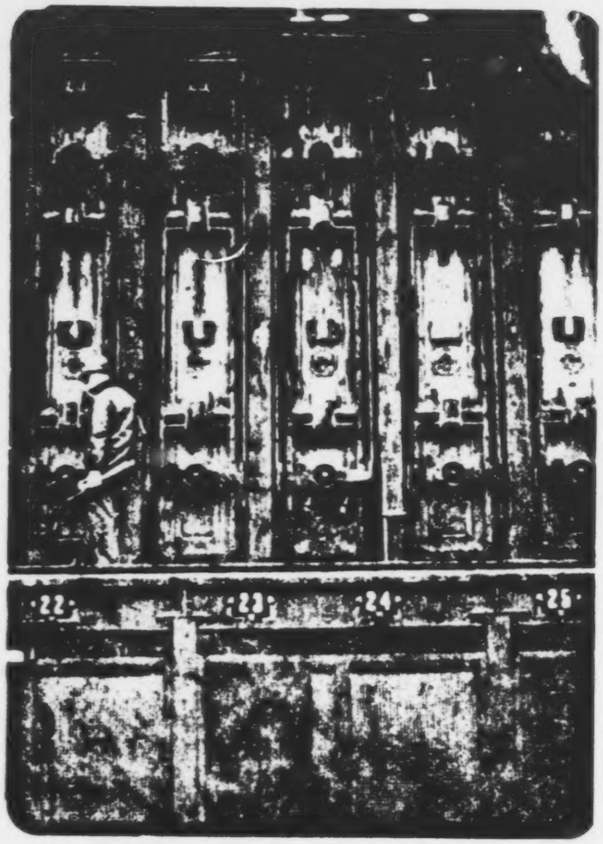

FIGURE 5. NO. 6 COKE OVEN SHOWING
EIGHT THERMOCOUPLE LOCATIONS

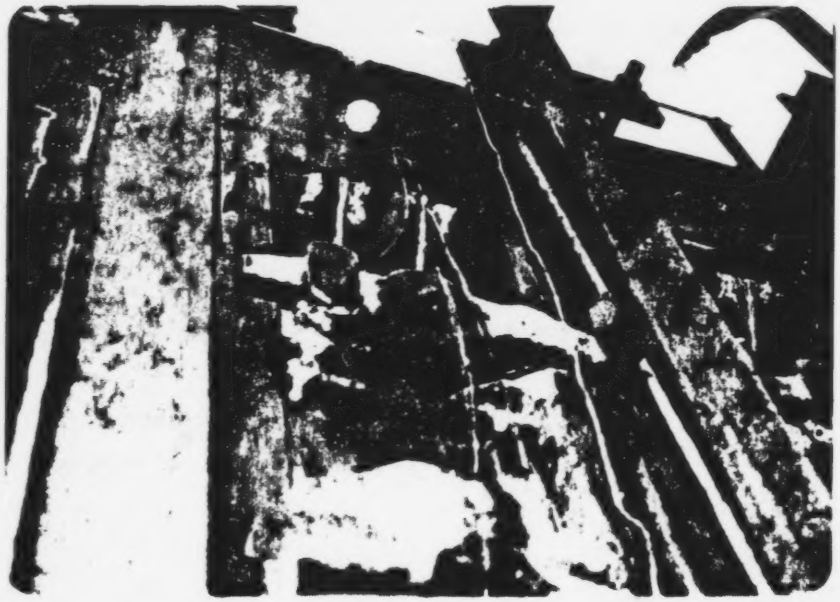

FIGURE 6. TOP PLATE OF SAMPLING HOOD INSTALLED ON NO. 6 COKE OVEN SHOWING THERMOCOUPLE LEADS AND PURGE AIR PIPE IN PLACE

thermocouple installations. The couples were 20 gage Chromel-alumel wires joined by a welded bead. At the point on the door where temperature was to be read, a small hole about 0.3 cm (1/8 inch) deep was drilled. A thermocouple was inserted in the hole and the bead was peened with a center punch so as to fill the hole and make the couple secure. To further secure the couple a spot several inches from the couple bead was cleaned by abrasion and a stainless steel foil strap was welded over the insulated couple wires. In Figures 3, 4, and 5, the cleaned spots can be seen as bright strips. Best detail appears in Figure 4 which also shows in good detail the disconnect plug that enabled thermocouple lead wires to be quickly pulled up out of the way when the door had to be removed to push the oven.

Figure 6 shows thermocouple leads passing up through the gas exit in the sampling-hood top plate. Figure 7 is a general view of the 12 point Honeywell recorder in position on top of the battery. Figure 8 is a closeup of the recorder that shows the general trace of temperatures being recorded. Since only eight temperature points were being measured in the door, the remaining four (Nos. 9, 10, 11, and 12) were shorted in the back of the recorder; thus, they recorded air temperature in the back of the recorder.

A record of ambient temperature in the area was obtained from the Huntington, West Virginia, weather service, located 30 miles east and 23 miles south of the Portsmouth, Ohio, coke-oven battery. Table 2 summarizes these temperatures from 1:00 p.m., April 24, through 1:00 p.m. on April 25.

The thermocouple installation was completed on No. 6 oven door the morning of April 24. The push on No. 6 oven was completed at 2:07 p.m. and the door was back in place at 2:08 p.m. Thermocouple leads were reconnected and recording was started at 2:15 p.m., April 24. The oven was charged at 2:28 p.m. and this charge was pushed at 5:35 a.m. on the morning of April 25.

Although door temperature measurements with the hood in place were not a previously planned part of this program, time and equipment

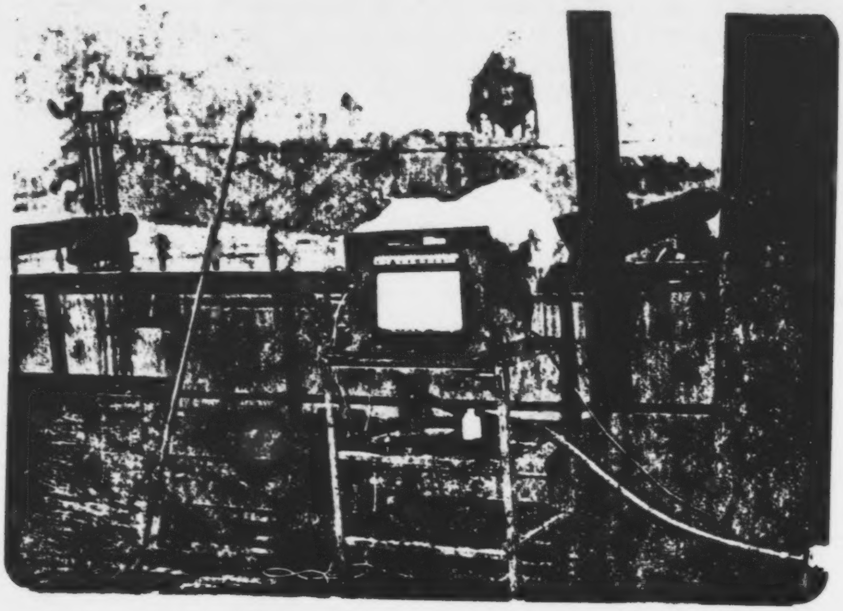

FIGURE 7. TWELVE POINT RECORDER INSTALLED ON TOP OF BATTERY ABOVE NO. 6 OVEN

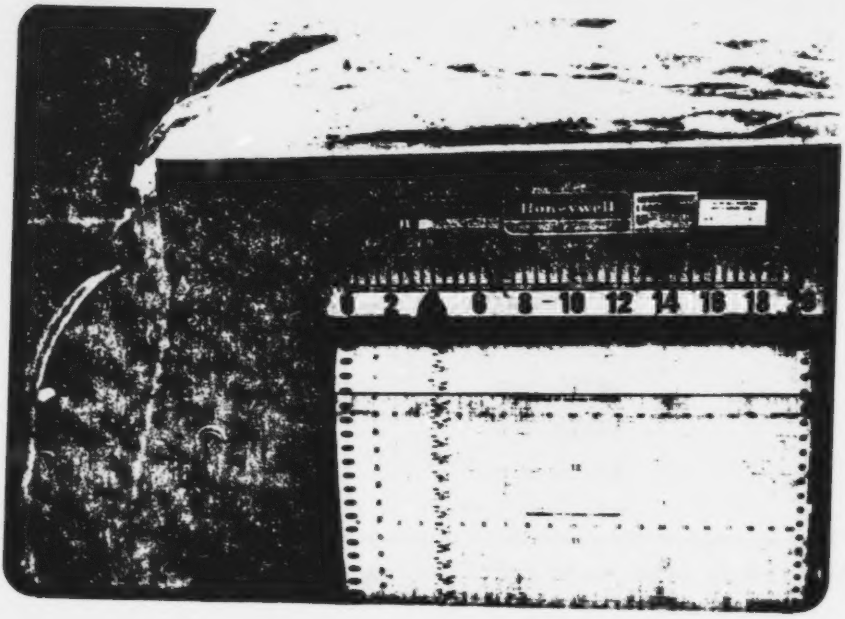
Honeywell
0 2 6 8 10 12 14 16 18

FIGURE 8. CLOSEUP OF TEMPERATURE RECORDER

TABLE 2. AMBIENT TEMPERATURE IN PORTSMOUTH AREA DURING PERIOD OF COKE-OVEN DOOR TEMPERATURE MEASUREMENTS (APRIL 24-25, 1975) AS RECORDED BY HUNTINGTON, WEST VIRGINIA, WEATHER SERVICE(a)

	Time	Temperature, C	Temperature, F
Thursday, April 24	1:00 p.m.	17.2	63
	2:00 p.m.	17.2	63
	3:00 p.m.	17.2	63
	4:00 p.m.	17.2	63
	5:00 p.m.	17.8	64
	6:00 p.m.	17.2	63
	7:00 p.m.	17.2	63
	8:00 p.m.	16.7	62
	9:00 p.m.	16.7	62
	10:00 p.m.	16.7	62
	11:00 p.m.	15.6	60
	12:00 a.m.	14.4	58
Friday, April 25	1:00 a.m.	13.3	56
	2:00 a.m.	13.3	56
	3:00 a.m.	12.8	55
	4:00 a.m.	12.8	55
	5:00 a.m.	13.3	56
	6:00 a.m.	13.3	56
	7:00 a.m.	13.9	57
	8:00 a.m.	14.4	58
	9:00 a.m.	15.0	59
	10:00 a.m.	16.1	61
	11:00 a.m.	16.1	61
	12:00 p.m.	15.6	60
	1:00 p.m.	17.2	63

(a) Located 30 miles east and 23 miles south of coke oven battery.

were available so several hours of temperature measurements were made under sampling-hood conditions.

No high-volume sampler and filters were used in these test runs. Since only door temperatures were of interest, purge air and door emissions merely exhausted through the hood top plate to the atmosphere.

Results of Test Runs

Table 3 presents a summary of average door-temperature values, without the sampling hood, during a 15-minute period before charging and after the door had been put on. It also gives the average temperature value for each of the eight thermocouples during the complete coking cycle for the April 24-April 25, 15-hour period.

Figure 9, plotted over the span of three pages, shows the curves for temperature plots of couples No. 5, 6, 7, and 8. Only temperatures from the four couples on the right side of the door were plotted because the right side of the door was consistently the hottest side. Figure 9 shows that the hottest spot was at couple No. 7. It started out at about 199 C (390 F), gradually increased to a maximum of about 213 C (416 F) after 5 hours, leveled off to 209 C (409 F) for about 1.5 hours and then very gradually decreased to around 199 C (390 F) at the end of the coking cycle. Couple No. 6 leveled off and started to decline in temperature more quickly than No. 7. No. 5 and No. 8 declined near the start of the cycle and leveled off after about 3.5 hours.

Figure 10 is a plot of temperatures from thermocouples 5, 7, and 8 with the sampling hood installed and immediately after the hood is removed. It shows temperatures with the hood in position for 2 hours and 20 minutes, and the temperature decrease over a period of an hour after the hood was removed. The plot of No. 7 couple in Figure 10 indicates that temperature falls more rapidly when the hood is removed than it rises when the hood is installed. Theoretical analysis discussed later shows a good correlation between the 241 C (465 F) maximum temperature recorded with the hood in place and the calculated value of 248 C (478 F) at a purge air rate of 1.7 m^3/min (60 ft^3/min).

TABLE 3. AVERAGE DOOR TEMPERATURES WITHOUT HOOD DURING EMPTY OVEN PERIOD AND OVER A COMPLETE 15-HOUR COKING CYCLE

Period Covered	Average Temperature, C and F Thermocouple Number 1	2	3	4	5	6	7	8
4/24/75, 2:15 - 2:30 p.m.: Empty Oven	181 357	181 357	189 373	182 360	182 360	191 375	201 394	171 340
4/24, 2:28 p.m.- 4/25, 5:35 a.m.: Complete 15-Hour Coking Cycle	170 339	172 342	195 383	174 345	171 340	186 368	206 403	162 324

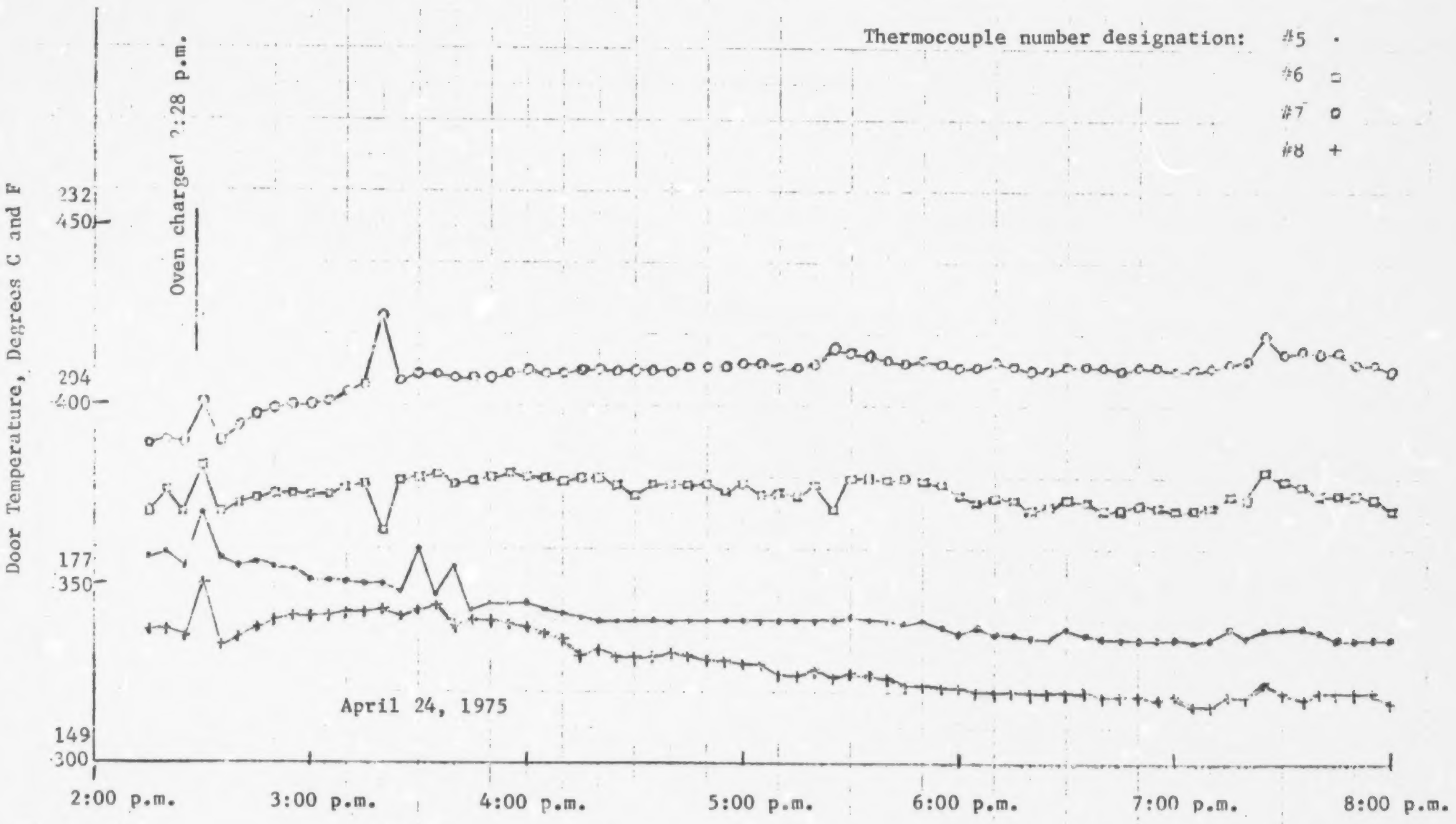

FIGURE 9. TEMPERATURE RECORD OF FOUR THERMOCOUPLES, WITHOUT HOOD, RIGHT SIDE OF NO. 6 COKE-OVEN DOOR, APPROXIMATE 15-HOUR CYCLE, APRIL 24-25, 1975

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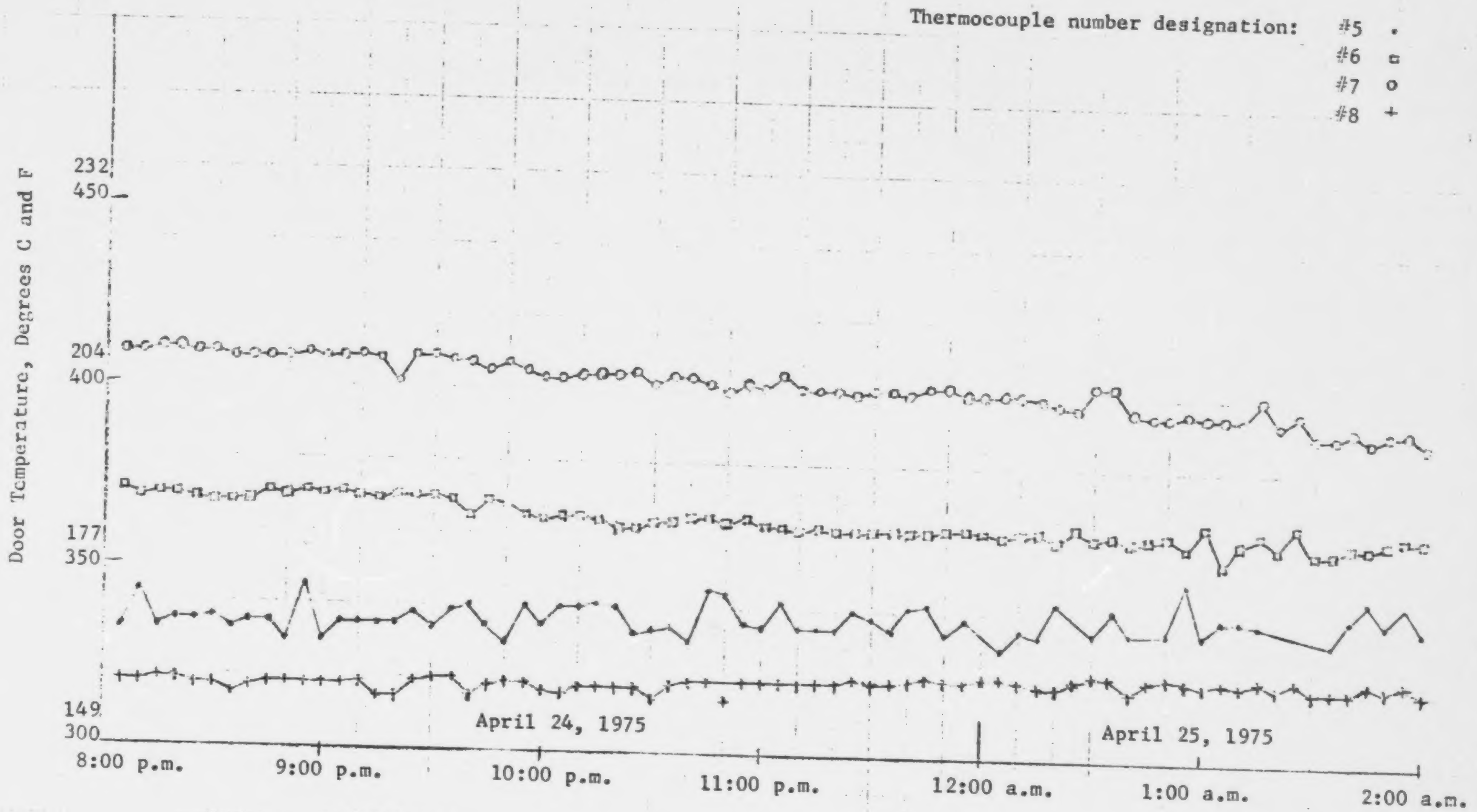

FIGURE 9. (Continued)

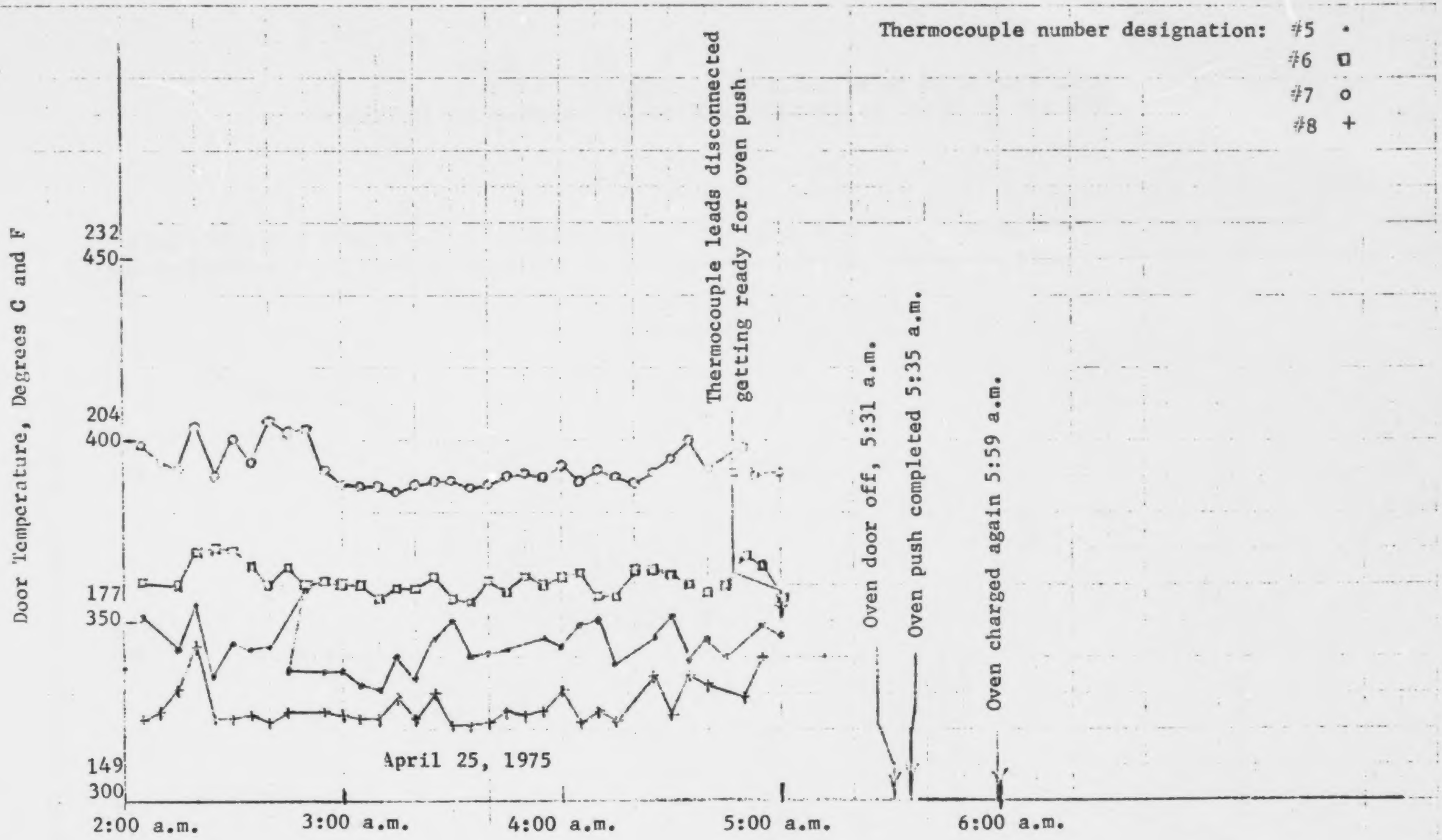

FIGURE 9. (Continued)

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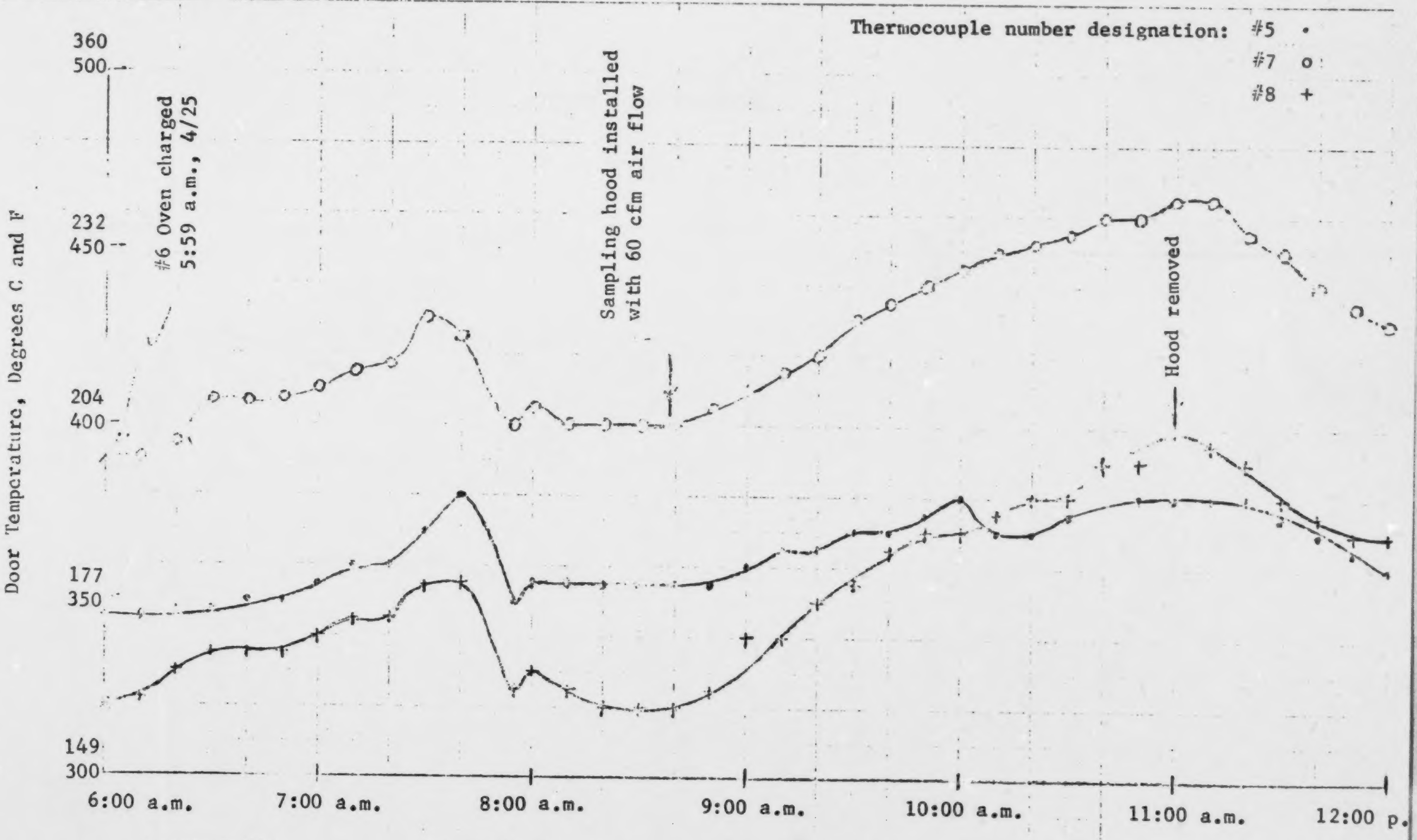

FIGURE 10. TEMPERATURE RECORD OF THERMOCOUPLES NO. 5, 7, and 8, WITH SAMPLING HOOD IN PLACE FOLLOWING NO. 6 OVEN PUSH, APRIL 25, 1975

Theoretical Analysis

A parametric analysis was conducted to determine the effectiveness of potential modifications to reduce the temperature of the coke-oven door with the hood in place. However, first it was necessary to determine the thermal condition of the door under normal operating conditions. Using the temperature data obtained in the field test, the proportion of heat loss due to natural convection and radiation and the thermal resistance of the door were determined. Quasi-steady-state, one-dimensional, thermal analyses were then performed with the hood in place to determine the predicted increase in door temperature with the original testing hood. Finally, the effect on temperature and heat flux was determined parametrically over a range of purge-gas flows and emissivities with the insulation removed. A theoretical analysis of the transient behavior of the door following hood removal was not conducted due to potential complexity. However, the transient behavior was determined by an additional test conducted following the normal operation cycle and is described elsewhere in this report.

Calculation Procedure

In order to keep the analysis essentially one-dimensional, it was necessary to chose a location on the door at which the calculations would be performed. (An alternate procedure would be to use averages over the entire door, but this was rejected as combining and masking too many different effects such as purge gas temperature rise and end effects.) The location used was thermocouple location No. 7 which is 2.67 meters (8-3/4 feet) from the bottom of the door. This was chosen because it was farthest from end effects and away from latches which act as cooling fins and further complicate the analysis. Thus, it was the maximum temperature recorded. In addition, it had the best defined flow because the upward flow at that location had been unobstructed for approximately 1.2 meters (4 feet) below.

In order to be quasi-steady-state, the average of the temperature at location No. 7 over the entire cycle, 206 C (403 F), was used as the basis for the normal operation calculations. From this temperature and an average ambient temperature, 15.6 C (60 F), the normal operation heat fluxes at this location were calculated using accepted heat-transfer correlation from McAdams(a). The natural convection heat flux from a vertical plate was 1379 w/m^2 (437 Btu ft^{-2} hr^{-1}) and was in the turbulent regime so that the characteristic length cancelled out of the correlation. The radiation using a door emissivity of 0.6 and a view factor of 1.0 was 1562 w/m^2 (495 Btu ft^{-2} hr^{-1}). This gave a total heat flux of 2941 w/m^2 (932 Btu ft^{-2} hr^{-1}).

To calculate the effect of the hood installation and other changes, it was assumed that the average inside wall surface temperature would not be affected by the changes since it is essentially fixed by the process. To determine this steady-state inside-surface temperature, the one-dimensional thermal resistance of the door was calculated from available thermal conductivity data. The door consisted of 34.3 cm (13-1/2 in.) of first quality silica firebrick with a thermal conductivity of 190 w/m K(b) (1.10 Btu ft^{-1} hr^{-1} F^{-1}) plus 5.1 cm (2 in.) of H.B. #28 castable refractory with a conductivity of 0.38 w/m K (0.22 Btu ft^{-1} hr^{-1} F^{-1}) for a total thermal resistance of 0.3146 m^2Kw^{-1} (1.785 hr ft^2F Btu^{-1}). This gives a calculated inside-surface temperature of 1131 C (2067 F) which was held fixed for all subsequent calculations. This wall surface temperature is within the range of 1010 to 1149 C (1850 to 2100 F) given by Preston(c) for typical coking operation.

For all calculation with the hood in place, steady-state heat balances were performed on the hood and at the door surface. The heat transferred through the door was convected to the purge air and radiated to the hood. The heat received by the hood was radiated and convected to the outside ambient air as well as some additional convection to the purge air. Then insulation was added on the hood, inside and outside hood temperatures were calculated and the temperature difference determined by the heat flux to the ambient and the thermal resistance of the insulation. The purge air temperature rise was also calculated using total heat convected to the purge-air from the inlet to location No. 7. The temperature differences at location 7 were used in this calculation. Although the door wall, hood, and air temperatures all decrease in the direction of the inlet at the bottom, the temperature differences should remain nearly constant, so use of location 7 temperature differences is a reasonable approximation. Iterations were performed on the various temperatures until all the heat balances and other conditions were satisfied.

(a) McAdams, W. H., Heat Transmission, 3rd Edition, McGraw-Hill, New York, 1954.

(b) w = watts; m = meter; K = degrees Kelvin.

(c) Preston, E., "Carbonization of Coal and Gas Making", Mechanical Engineers' Handbook, Edited by L. S. Marks, 5th Edition, McGraw-Hill, 1951, p 817.

The convection to the purge air flow was a combination of natural and forced convection. The Reynolds number for the purge air flow in the unobstructed passage was 1800 to 6100 which is in the transition regime from laminar to turbulent flow. Therefore, the transition correlation of Kroll given in McAdams(a) was used. However, the natural convection heat transfer coefficient for vertical surfaces was always much larger than the forced convection coefficient. For combined natural and forced convection in laminar flow, Martinelli and Boelter(b) derived and confirmed a relationship of the form

$$h_{combined} = \sqrt[3]{h^3_{natural} \pm h^3_{forced}} .$$

This relationship was used to combine the convection in the present calculations although the flow was in the transition regime. Because the natural convection h was larger than the forced h, the effect on h directly of increasing purge air flow was quite small. However, the increased air flow decreased the air temperature rise which did increase the temperature difference and the natural convection h so that there was an effect of purge-gas flow rate.

(a) McAdams, loc. cit., p. 240.

(b) Martinelli, R. C. and Boelter, L.M.K., University of California Publication in Engineering, Vol. 5, No. 2, Berkeley, 1942, pp. 23-58.

Results

Table 1 shows a summary of results of the various cases calculated. The emissivity of 0.2 is representative of the aluminum hood or aluminum foil used with the original hood. The emissivity of 0.9 is representative of black paint on the aluminum hood. All the results apply to thermocouple location No. 7 and, therefore, are approximately the maximum to be expected. The total heat flux as well as the division between the heat transferred to the purge air and the ambient are also given. All the various terms in the heat balances were calculated and are available in the detailed calculation sheets.

Figure 11 shows the calculated maximum door temperature versus purge-gas flow rate for the various cases. It does not appear possible to decrease the door temperature to the normal operating temperature of 260 C (403 F) by increasing the purge-gas flow rate or the emissivity of the surfaces. Painting the outside only has little effect on decreasing the door temperature. On the other hand, painting the inside only has a significant effect. The predicted value of 248 C (478 F) for both sides painted and a purge-gas flow rate of 1.7 m^3/min (60 cfm) is close to the value of 241 C (465 F) measured in the test of the No. 7 thermocouple which had not yet quite reached its quasi-steady-state value after about 2 hours with the hood on.

Figure 12 shows the calculated maximum hood temperature versus purge-gas flow rate for the same cases. With equal emissivity the maximum hood temperature is not very dependent on purge-gas flow rate or the emissivity itself. However, there are significant changes with unequal emissivities.

Figure 13 shows the total heat flux dissipated and the division between heat transfer to the purge air and to the ambient for the cases with equal emissivities of 0.9 only. The total heat flux has decreased very little from the normal operation value of 2953 w/m^2 (936 Btu $ft^{-2}hr^{-1}$) and is nearly independent of purge gas flow rate.

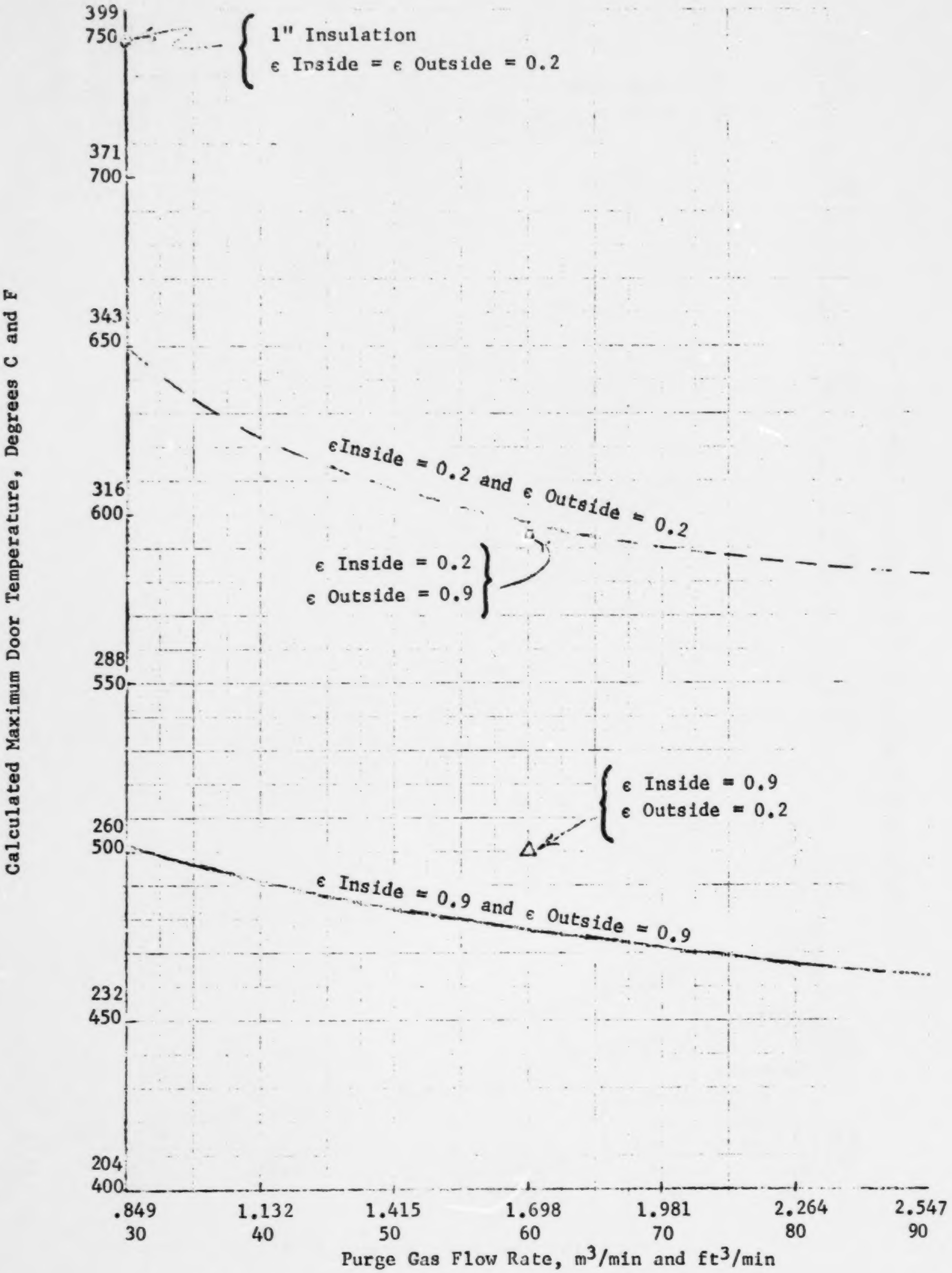

FIGURE 11. CALCULATED MAXIMUM DOOR TEMPERATURE
VERSUS PURGE-GAS FLOW RATE

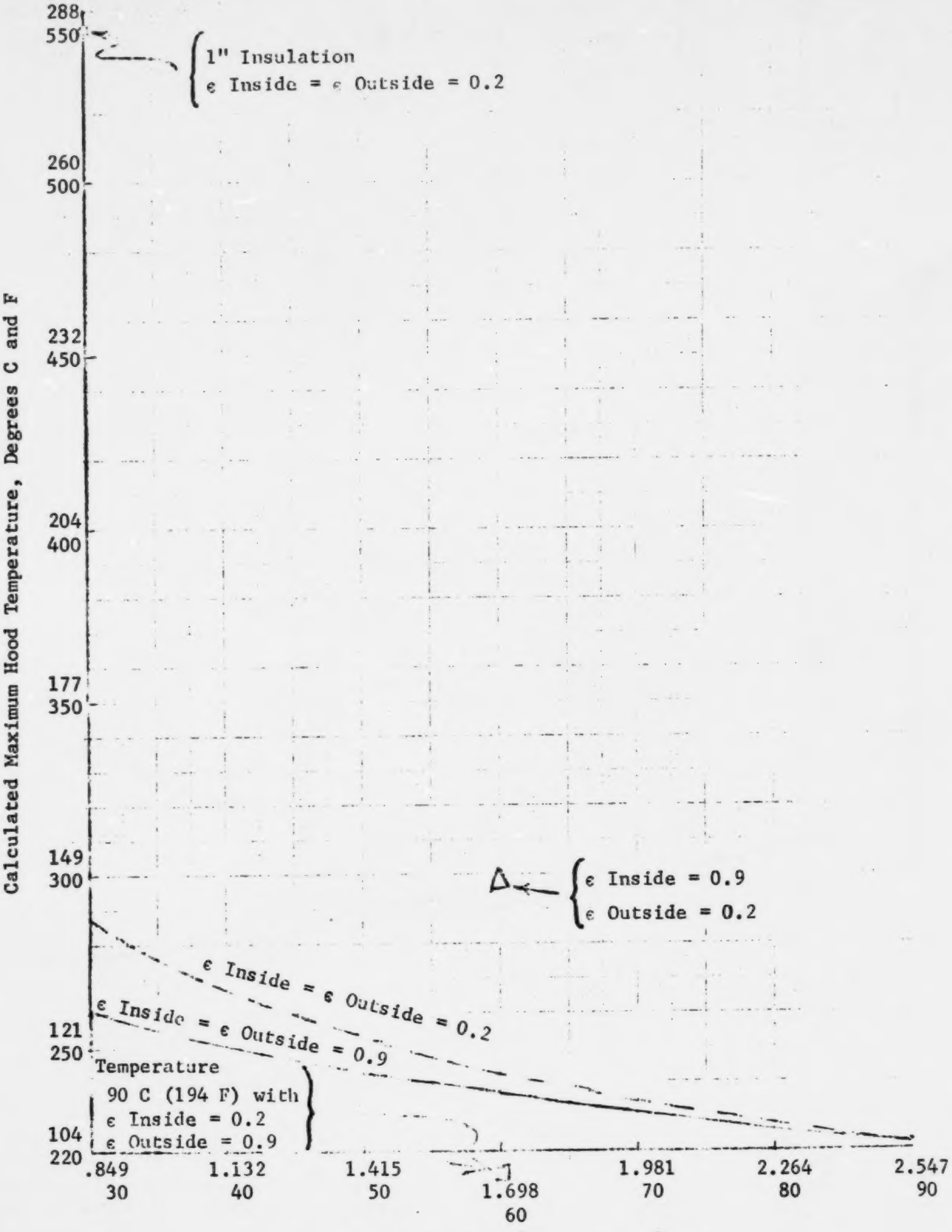

FIGURE 12. CALCULATED MAXIMUM HOOD TEMPERATURE VERSUS PURGE-GAS FLOW RATE

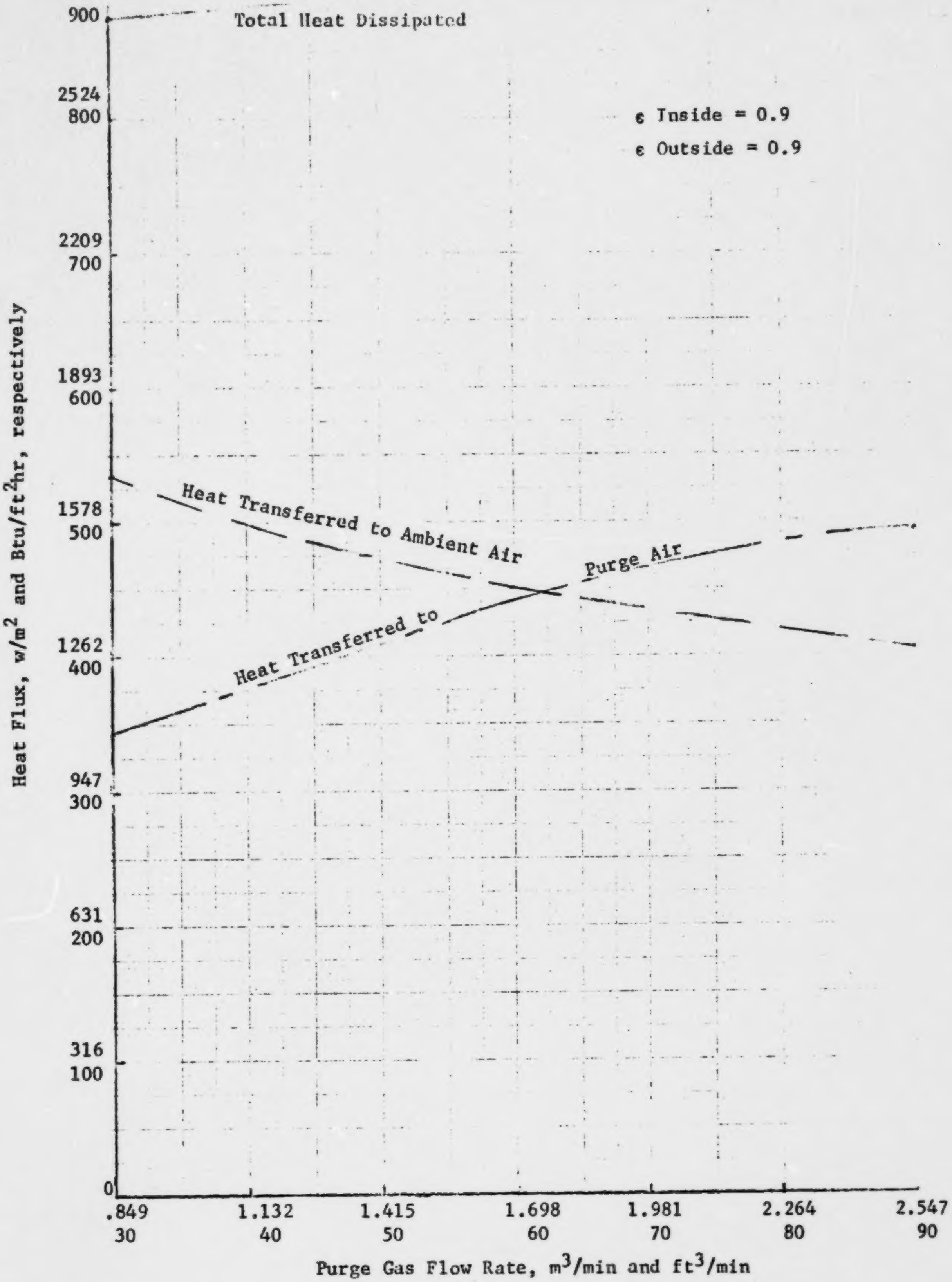

FIGURE 13. TOTAL HEAT FLUX DISSIPATED AND DIVISION OF HEAT FLUX BETWEEN PURGE AND AMBIENT AIR

APPENDIX B

HEAT TRANSFER ANALYSIS FOR HOOD

SUMMARY REPORT

on

EFFECT OF FINS ON COKE-OVEN HOOD HEAT TRANSFER

to

ENVIRONMENTAL PROTECTION AGENCY

October 9, 1975

by

G. R. Whitacre

BATTELLE
Columbus Laboratories
505 King Avenue
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INTRODUCTION

To permit sampling of emissions from coke-oven doors, a hood must be used to contain the emissions. The addition of a hood in the vicinity of the coke-oven door serves to reduce heat loss from the door and, thus, increases the door temperature. It has been proposed that fins might be added to the hood to increase heat loss from the hood and thereby, reduce the temperature of the hood and of the door. A thermal analysis was conducted to determine the effectiveness of hood fins and whether they should be placed on the inside or outside of the hood. In addition, optimum fin spacing and heights were determined.

CALCULATION PROCEDURE

The analytical thermal analysis techniques described in a previous report* were used to predict steady state maximum door and hood temperatures. Only the modification and additions necessary to include the effect of the fins and optimize their spacing and height are discussed here. There are two limiting analysis procedures available to handle natural convection fin heat transfer. One limit applies to small fins which are spaced far enough apart that the boundary layers which form around one fin do not interact with the boundary layers from the adjoining fins. In addition, it is assumed (for vertical fins) that the heat transfer coefficient on the fin surfaces including the corners is the same as the coefficient on the plane base surface. This heat transfer coefficient is determined from a Grashof number correlation based on vertical hood height. The only effect of the fins is to increase the surface area for heat transfer. However, the fin surface area is multiplied by the fin effectiveness due to heat conduction in the fin before this product is added to the remaining base area to obtain the effective total area for heat transfer. For aluminum fins with the same gage as the hood (16) the fin effectiveness was over 99 percent for all the cases analyzed.[*] Therefore, fin thickness could be changed with practically no effect on fin effectiveness.

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*Whitacre, G.R., Miller, S.E., and Purdy, J.B., "Thermal Analysis of Coke Oven Doors", Summary Report to EPA, June 12, 1975.

For this limiting case of small fins with no interaction, the natural convection is in the turbulent regime on both sides of the hood. Although the purge flow on the inside of the hood enclosure is provided at a rate of 1.7 m^3/min (60 ft^3/min), natural convection is still the dominant mode of heat transfer and the procedure used in combining the forced and natural convection is described in the previous report. Essentially the heat transfer coefficient is determined by the turbulent natural convection but the purge air temperature rise affects the heat transfer by reducing the available temperature difference. The analysis procedure used to determine the fin effectiveness for this limiting case is identical to that described in the previous report.[**] The surface area on both the inside and outside of the hood was increased in steps representing the addition of fins, and new wall, hood, and air temperatures were determined by performing iterative calculations until the energy (heat balance) equations were satisfied.

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[*] Fin effectiveness is defined as the ratio of the amount of heat dissipated by the fin surface to that which would be dissipated if the fin surface were held at the temperature of the fin base.

[**] Ibid.

The other limiting case for vertical natural convection fins is to consider the flow between the fins as flow in an enclosure with constant wall temperature. (For aluminum fins the high fin effectiveness is equivalent to a constant wall temperature.) This case has been well analyzed both experimentally and analytically by Elenbaas for both parallel plates* and for enclosures of various shapes and aspect ratios.** In addition Elenbaas derives an expression to optimize the fin spacing for maximum heat transfer as a function of aspect ratio of the enclosure. This optimum results from a decrease in the heat transfer coefficient as the fin spacing decreases in competition with an increase in the surface area with decreased spacing. Treating the space between the fins as an enclosure, the optimum fin spacing is given by

$$\frac{r_m}{l} \quad Gr_m \, Pr = 0.72 \, (\Psi Re)^{4/3} \quad ,$$

where

r_m = hydraulic radius with optimum spacing

l = vertical distance

Gr_m = Grashof number based on r_m^3

Pr = Prandtl number of fluid.

The flow resistance parameter Ψ Re is a function of the aspect ratio and varies from 24 for an infinite parallel plate to 14.225 for a rectangular enclosure with an aspect ratio of 1.0. The complete variation with aspect ratio is given in the second Elenbaas paper.

In calculating the effect of fins in the enclosure limit, various aspect ratios were selected and the optimum spacing calculated by the Elenbaas formula. In order to simulate a full enclosure for this limiting case, the aspect ratio was assumed to be equal to the ratio of twice the fin height to the distance between the fins. Physically, this assumption is equivalent to the actual fins with no leakage flow in or out past the plane of the fin tips. Also, the hydraulic radius as used by Elenbaas is twice the cross-sectional area divided by the wetted perimeter. This hydraulic radius is twice the value normally used in classical treatments of flow in enclosures.

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* Elenbaas, W., "Heat Dissipation of Parallel Plates by Free Convection", Physica, Vol. 9, No. 1, January, 1942, pp 1-28.

** Elenbaas, W., "The Dissipation of Heat by Free Convection. The Inner Surface of Vertical Tubes of Different Shapes of Cross-Section", Physica Vol. 9, No. 9, September, 1942, pp 865-873.

After the optimum fin spacing was calculated for the various aspect ratios the heat-transfer coefficient was determined from the Elenbaas correlation at the optimum point. The correlation is

$$Nu_m = \frac{hr_m}{k} = 0.385\ (\Upsilon\ Re)^{1/3} \quad ,$$

where

Nu_m = is the Nusselt number at the optimum spacing

h = is the heat transfer coefficient and

k = is the thermal conductivity of the fluid.

The heat transfer rate obtained in this manner is based on the temperature difference between the fin and the inlet air temperature and the effect of the air temperature rise in the flow direction is included in the derivation and verification of the correlation. Because of the small spacing between fins and the interaction between boundary layers the flow remains in the laminar flow regime so the correlation and all the results calculated for the enclosure limit are for laminar flow.

Using the heat-transfer coefficients and optimum spacings calculated for the various aspect ratios, the heat balance iterations previously formulated were repeated with the various fin arrangements on both sides of the hood. For the fins on the outside, the procedure was essentially the same as described, but several changes were necessary for the fins placed on the inside. Because it was assumed that there was no flow through the plane of the fin tips the inside flow was divided into two parts. In order to calculate the flow between the fins the theoretical solution of Bodoia and Osterle* was used since it included a prediction of the amount of flow and also showed good agreement with the experimental data of Elenbaas. The heat transfer by convection from the door surface was determined using only the difference between the total purge air flow and flow between the fin since only this flow was available to cool the door directly.

The fins also affect the radiation heat transfer by increasing the effective emissivity of the surface through the cavity effect. This increase in emissivity was included using the data from Sparrow and Gregg.**

RESULTS

Table 1 shows a summary of results for the various fin configurations considered. All of these results were obtained for an assumed purge air flow of 1.7 m^3/min (60 ft^3/min) and a hood emissivity of 0.9 (painted black) on both sides. The first line in the table repeats the results obtained previously (June 12, 1975 Summary Report) for the case without fins. Where an aspect ratio is given, the calculation procedure was based on the enclosure technique and the fin spacing is the optimized spacing (second limiting case discussed). Where no aspect ratio appears, no interaction was assumed and the area ratio was used to increase the appropriate heat transfer surface (first limiting case discussed). The total heat flux as well as the division between the heat transferred to the purge air and the ambient environment are also given. All the various terms in the heat balances were calculated and balanced by iteration and are available in detailed calculation sheets.

Figure 1 shows the calculated maximum door temperatures for various fin configurations. Somewhat surprisingly, the fins on the inside

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* Bodoia, J. R., and Osterle, J. F., "The Development of Free Convection Between Heated Vertical Plates", Journal of Heat Transfer, Trans. ASME, Series C, Vol. 84, No. 1, February, 1962, pp 40-44.

** Sparrow, E. M., and Gregg, J. L., "Radiant Emission from a Parallel-Walled Groove", Journal of Heat Transfer, Trans ASME, Series C, Vol. 84, No. 1, February, 1962, pp 40-44.

TABLE 1. SUMMARY OF RESULTS OF HEAT TRANSFER ANALYSIS

Total Area / Base Area	Fins Location	Spacing cm in	Height cm in	Enclosure Aspect Ratio	T_{Door} C F	T_{Door} C F	Heat Flux $\left\{\begin{matrix} w/m^2 \\ Btu/ft^2\ Hr \end{matrix}\right.$		
							q to Purge Air	q to Ambient	Total q
1.0	None	-	-	-	247.8	114.1	1389.1	1122.0	2811.1
					478.0	237.3	440.3	450.7	891.0
1.5	Inside	2.54	0.64	-	246.9	111.3	1429.5	1381.6	2811.1
		1.0	0.25		476.4	232.3	433.1	437.9	891.0
2.0	Inside	2.54	1.27	-	246.1	109.6	1464.6	1347.5	2812.1
		1.0	0.5		475.0	229.2	464.2	427.1	891.3
3.0	Inside	2.54	2.54	-	245.3	106.9	1520.1	1295.8	2815.9
		1.0	1.0		473.6	224.4	481.8	410.7	892.5
2.40	Inside	2.36	1.65	1.5	244.0	105.0	1564.2	1257.3	2821.5
		0.93	0.65		471.2	221.0	495.8	398.5	894.3
2.86	Inside	2.18	2.03	2.0	244.3	102.6	1607.8	1211.5	2819.3
		0.86	0.80		471.8	216.6	509.6	384.0	893.6
4.68	Inside	1.93	3.56	4.0	248.6	96.7	1701.2	1103.0	2804.2
		0.76	1.40		479.5	206.0	539.2	349.6	888.8
1.5	Outside	2.54	0.64	-	244.3	102.9	1331.4	1486.6	2818.0
		1.0	0.25		471.7	217.3	422.0	471.2	892.3
2.0	Outside	2.54	1.27	-	241.7	94.1	1290.1	1537.4	2827.5
		1.0	0.5		467.0	201.4	408.9	487.3	896.2
3.0	Outside	2.54	2.54	-	238.1	81.7	1234.9	1607.5	2842.4
		1.0	1.0		460.5	179.0	391.4	509.5	900.9
1.95	Outside	2.72	1.30	1.0	251.7	124.2	1430.8	1365.2	2796.0
		1.07	0.51		485.0	255.5	453.5	432.7	886.2
2.86	Outside	2.16	2.01	2.0	248.3	208.5	1395.8	1407.8	2803.6
		0.85	0.79		479.0	240.5	442.4	446.2	888.6
4.68	Outside	1.91	3.51	4.0	244.2	102.8	1330.8	1487.6	2818.4
		0.75	1.38		471.5	217.0	121.8	471.5	893.3

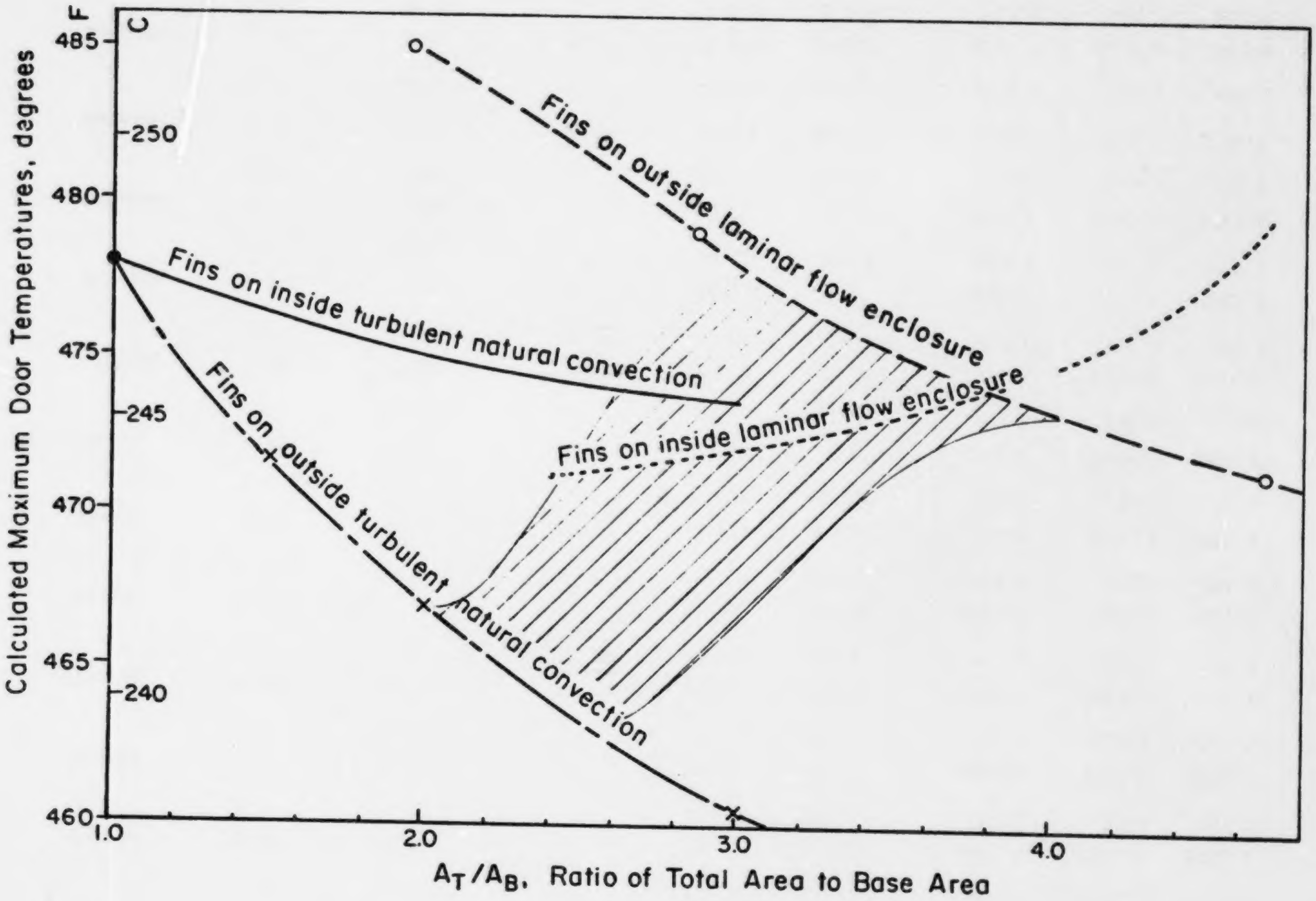

FIGURE I. CALCULATED MAXIMUM DOOR TEMPERATURE FOR VARIOUS FIN CONFIGURATIONS

had very little effect on the maximum door temperature. In fact, practically all of the slight decrease shown for fins on the inside with turbulent natural convection, i.e., the no interaction limit, was a result of the increase in effective emissivity caused by the cavity effect. As the ratio of the areas increases, the actual door temperature should switch from the no interaction limit curve to the laminar flow enclosure curve. The poor performance of fins placed on the inside of the hood can be explained by a combination of factors. First, the heat transfer from the door to the hood is radiation dominated and convection is only secondary. Second, the inside fins do increase the heat transfer to the purge air and decrease the hood temperature as shown in Table 1. However, because of the interactions between the hood, wall, and purge air heat balances there is a detrimental effect of the lower hood temperature which balances the heat transfer gain and can even result in an increase in door temperature. This gives a significantly lower heat transfer rate to the ambient both by radiation and natural convection from the outside of the lower temperature hood. In addition, the increased flow and heat transferred in the enclosure between fins reduces the available purge air flow and resulting natural convection directly from the door to the purge air. Thus, it appears that fins placed on the inside of the hood are not worth the cost and effort and may even be detrimental.

The results for fins placed on the outside of the hood are quite different, however. For the no interaction assumption with turbulent natural convection, there is a beneficial effect of decreasing door temperature with increasing fin area. There are no major counterbalancing effects although the heat flux to the purge air does decrease due to the lower wall and hood temperatures. This effect of outside fins with turbulent natural convection does not come close to reducing the door temperature to its normal operating temperature of 206 C (403 F) however.

When the limiting analysis of a laminar flow enclosure is applied to the outside fin case there is a significant shift in results with an increase in wall temperature (compared with the no fin case, $A_T/A_B = 1$) for area ratios less than about 3. This is caused by a much lower heat-transfer coefficient inside the enclosure with laminar natural convection than exists on a vertical surface with turbulent natural convection. This lower coefficient is not offset by the increased surface area until an area ratio of 3 is reached. This decrease in heat-transfer coefficient would be a real effect as the interaction of the flow between fins increases. The actual wall temperature curve probably leaves the turbulent curve somewhere between an area ratio of 2 to 2-1/2 and should blend into the laminar flow enclosure curve somewhere between an area ratio of 3 to 4 as shown by the shaded area in Figure 1. This transition is only an estimate so it appears that short fins with an area ratio no greater than 2.0 to minimize flow interaction and maintain turbulent flow are most desirable. The optimum spacing for an area ratio of 2 is approximately 2.54 cm (1.0 in) resulting in a fin height of 1.27 cm (0.5 in).

A recent paper by Pnueli* indicates that an improvement in heat transfer can be achieved by a moderate inclination from vertical for natural convection fins. The initial decrease in length for a number of fins terminating in the vertical edge increases the heat-transfer coefficient enough to more than offset the cosine law decrease in Grashof number. However, this effect is based on a heat-transfer coefficient varying with $1^{-1/4}$ which is true for laminar natural convection. For turbulent natural convection we are trying to insure in the present case the coefficient is independent of L and thus there is no gain (only the cosine law loss) by inclining the fins.

CONCLUSIONS

The conclusions from the heat transfer analysis on the effect of fins on coke oven door heat transfer are as follows.

Vertical fins placed on the inside of the sampling hood are not effective in reducing door temperature.

Short vertical fins placed on the outside of the sampling hood can reduce the door temperature by a maximum of approximately 6 C out of a total temperature rise of 42 C from the normal operating condition as indicated in the June 12, 1975, Summary Report.

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*Pnueli, David, "Optimization of Inclined Convective Fins", Journal of Heat Transfer, Trans ASME, Series C, Vol. 96, No. 4, November, 1974, pp 545-547.

Deep vertical fins on the outside can actually cause an increase in the door temperature because of the trapping of flow between fins and the resulting transition to laminar flow.

If fins are used on the outside of the hood they should be approximately 1.27 cm (0.5 in) high on 2.54 cm (1.0 in) spacing and can be the same gage as the hood.

For this case, inclination of the fins from vertical provides no increase in heat transfer.

APPENDIX C

FIELD DATA AND CALIBRATION SHEETS

(Copies of field data and calibration sheets may be obtained from R.C. McCrillis MD-62, US Environmental Protection Agency, Research Triangle Park, N.C. 27711)

APPENDIX D

RECONSTRUCTED GAS CHROMATOGRAMS, ELECTRON IMPACT IONIZATION MASS SPECTRA, AND METHANE IONIZATION MASS SPECTRA OF EMISSIONS FROM COKE OVEN DOORS

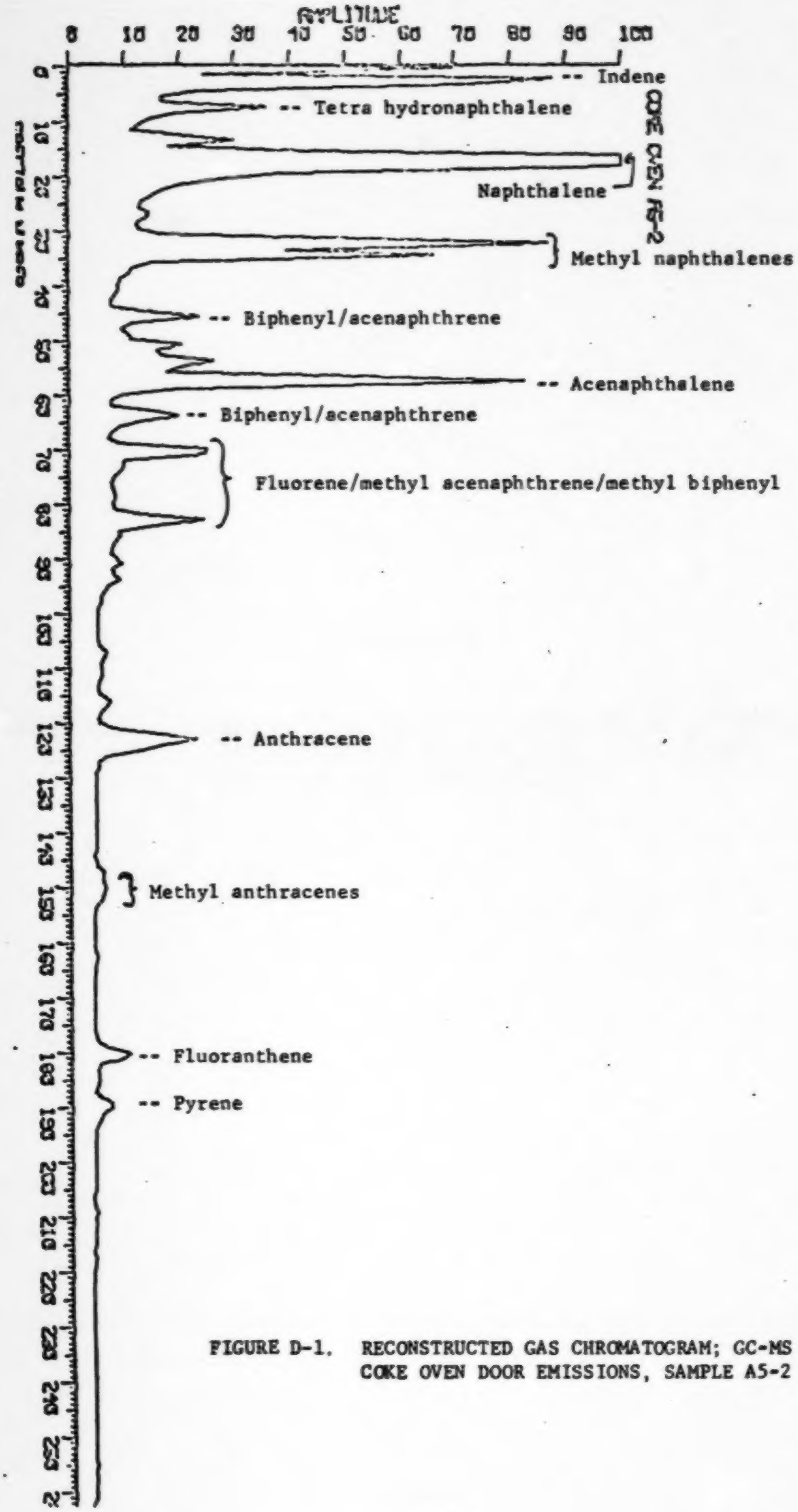
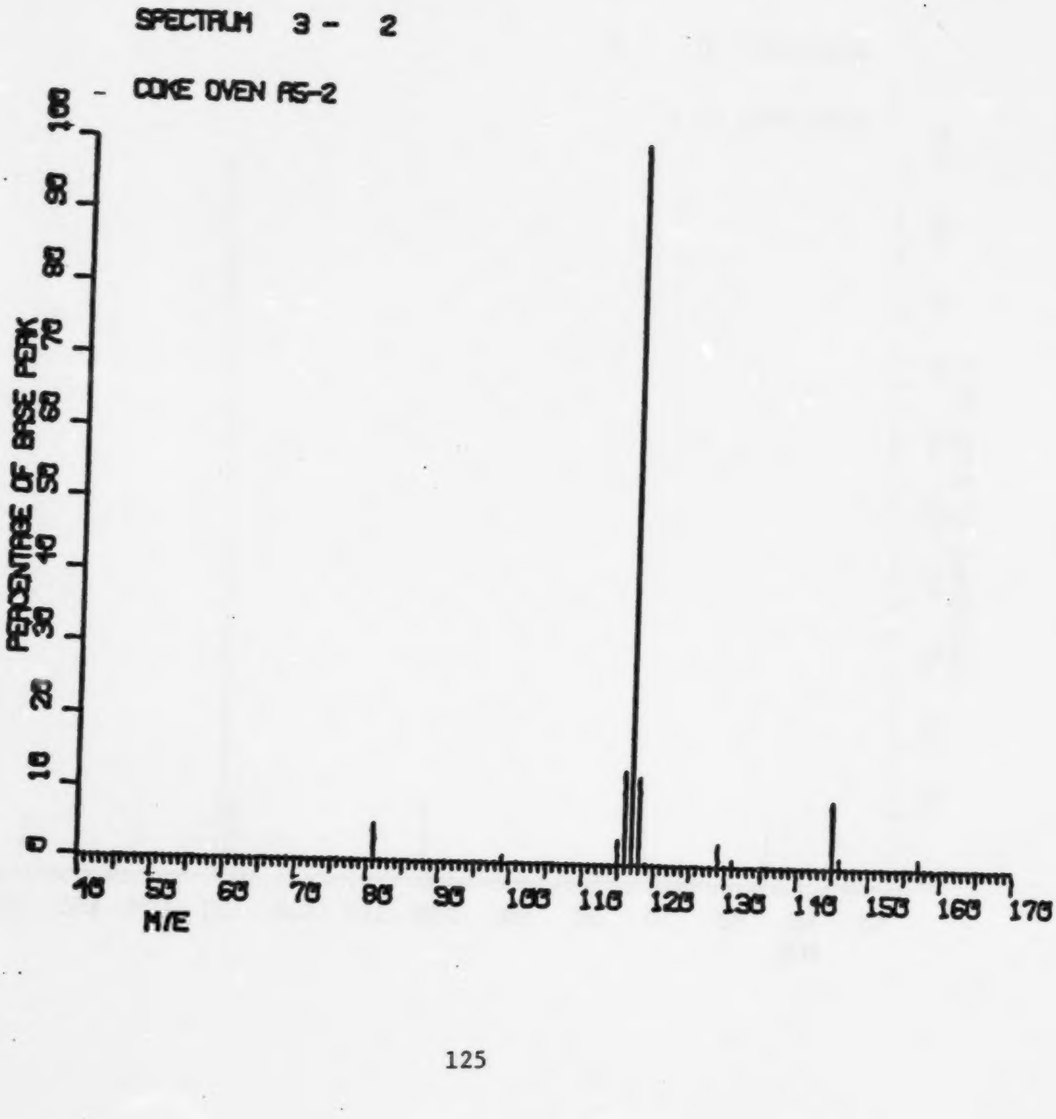
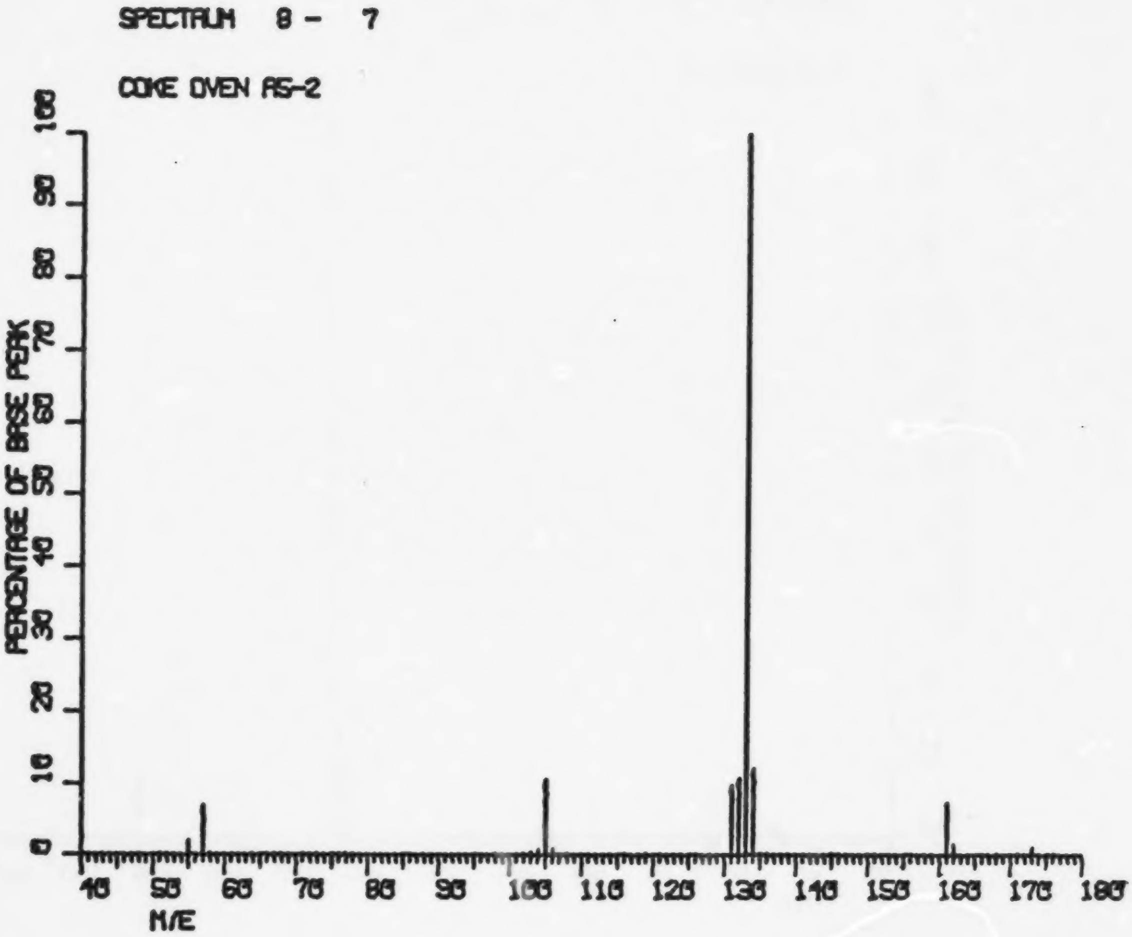
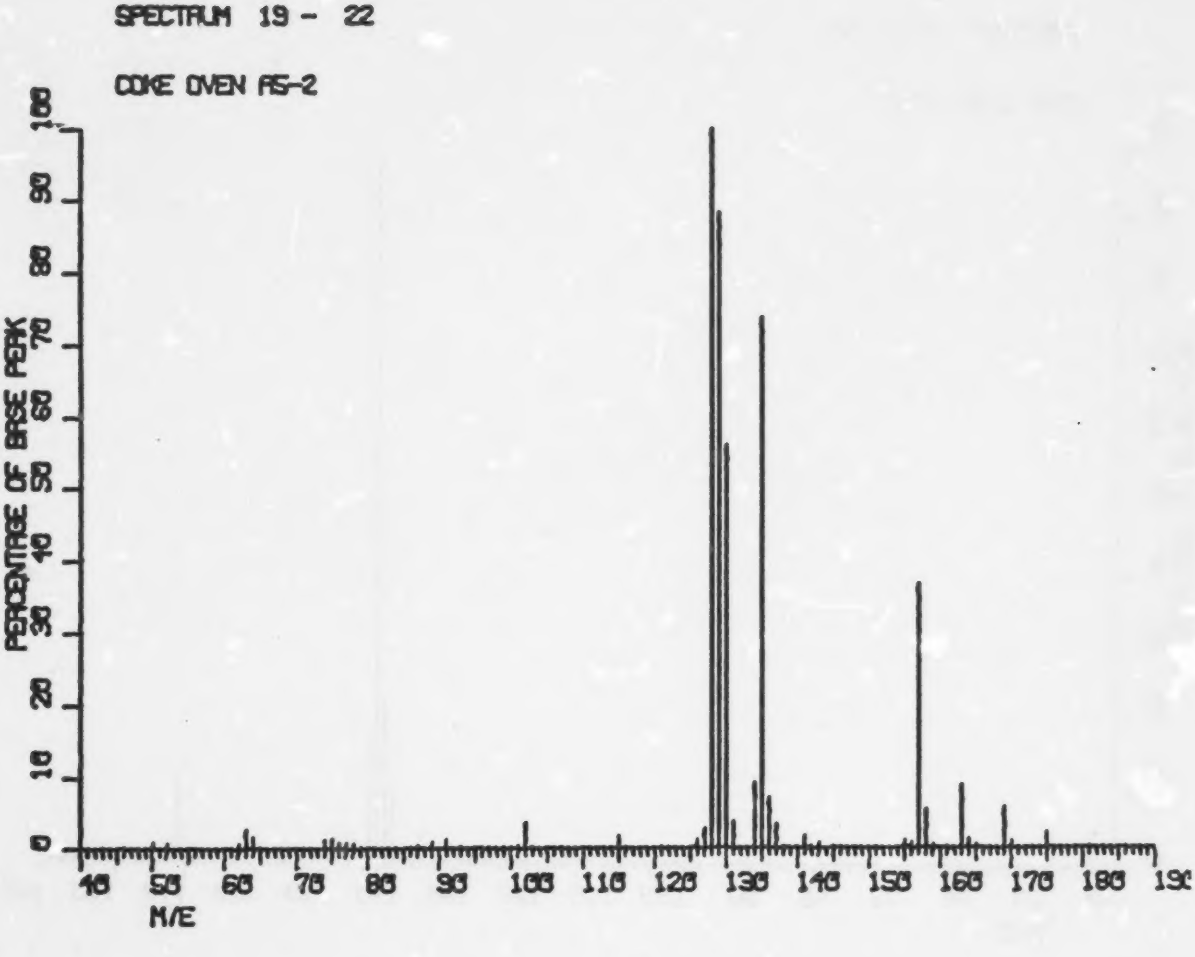


FIGURE D-1. RECONSTRUCTED GAS CHROMATOGRAM; GC-MS ANALYSIS OF COKE OVEN DOOR EMISSIONS, SAMPLE A5-2

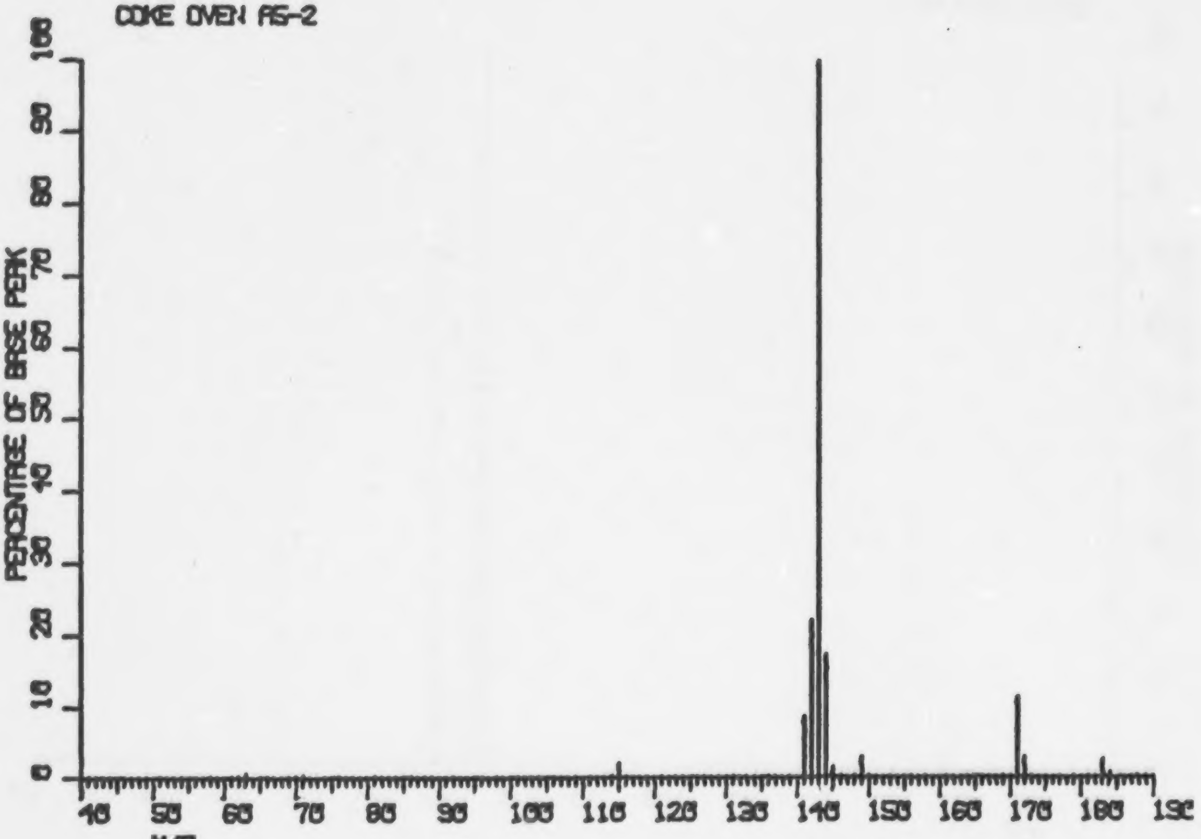

SPECTRUM 3 - 2
- COKE OVEN AS-2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
160
170
M/E


SPECTRUM 8 - 7
COKE OVEN AS-2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
M/E


SPECTRUM 19 - 22
COKE OVEN AS-2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
M/E

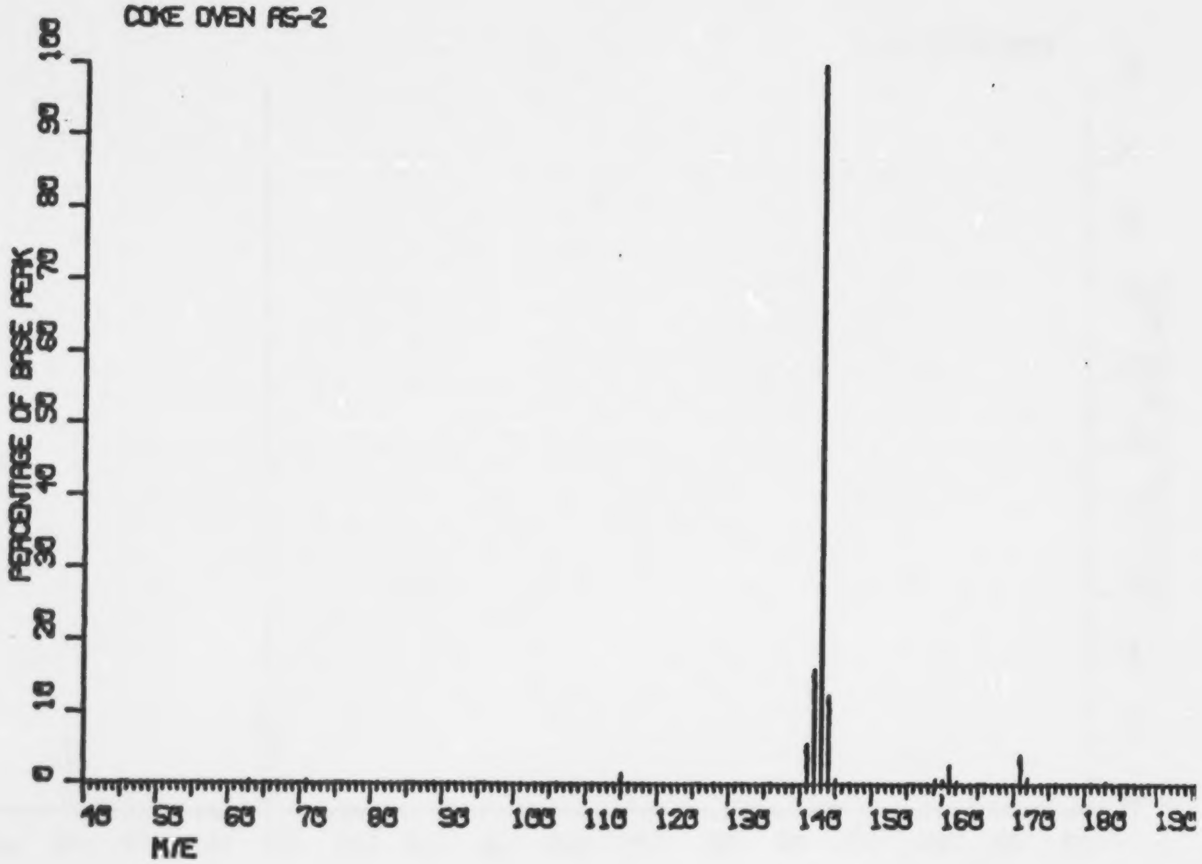
SPECTRUM 33 - 30

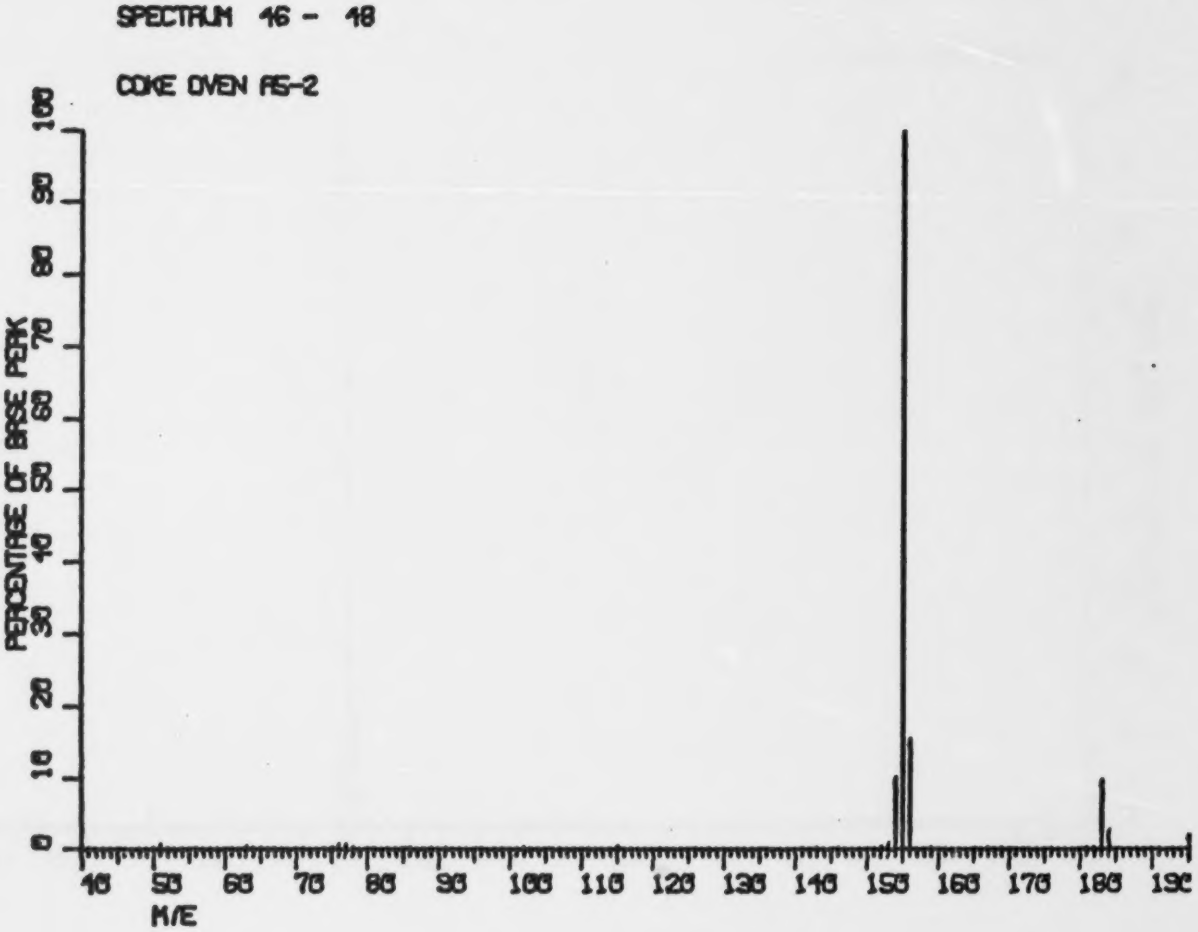
COKE OVEN AS-2



SPECTRUM 35 - 34

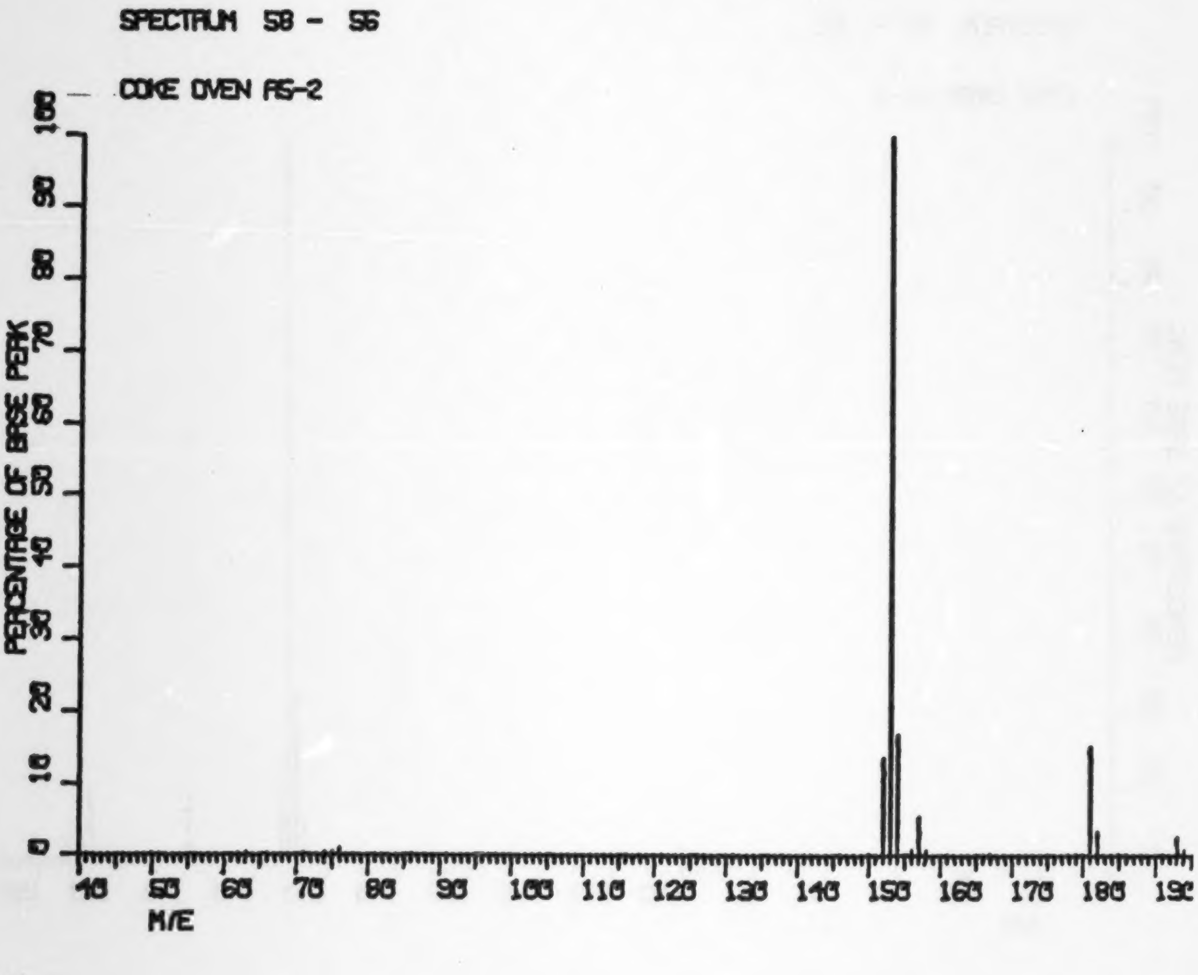
COKE OVEN AS-2

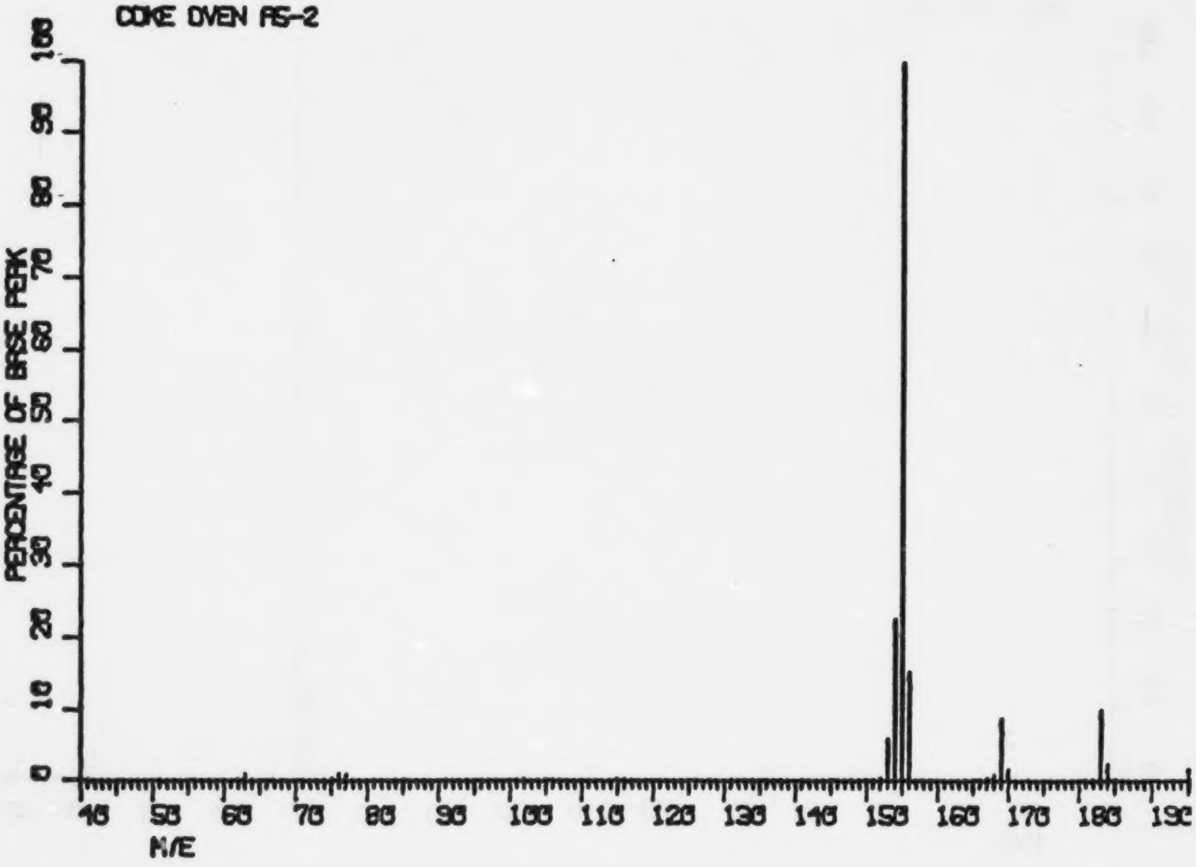




SPECTRUM 46 - 48

COKE OVEN AS-2


SPECTRUM 58 - 56
COKE OVEN AS-2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
M/E

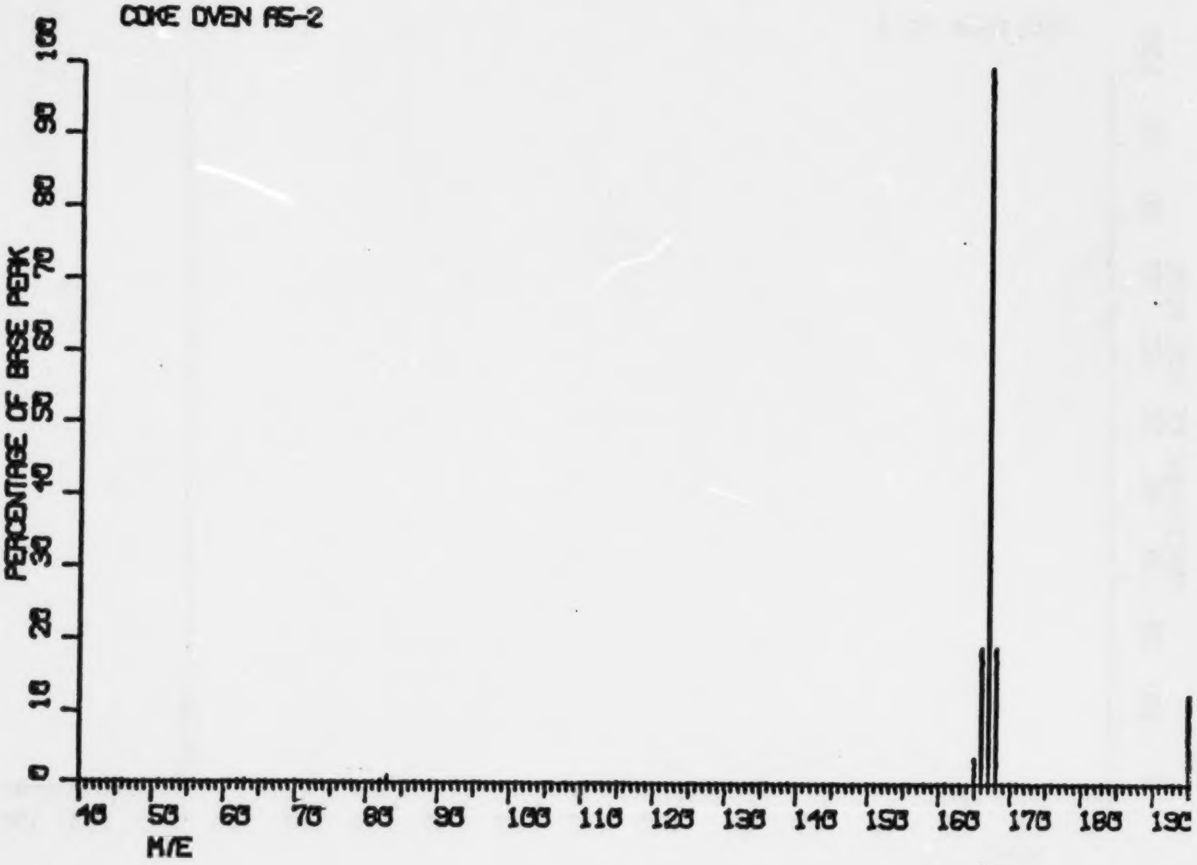


SPECTRUM 64 - 62

COKE OVEN AS-2

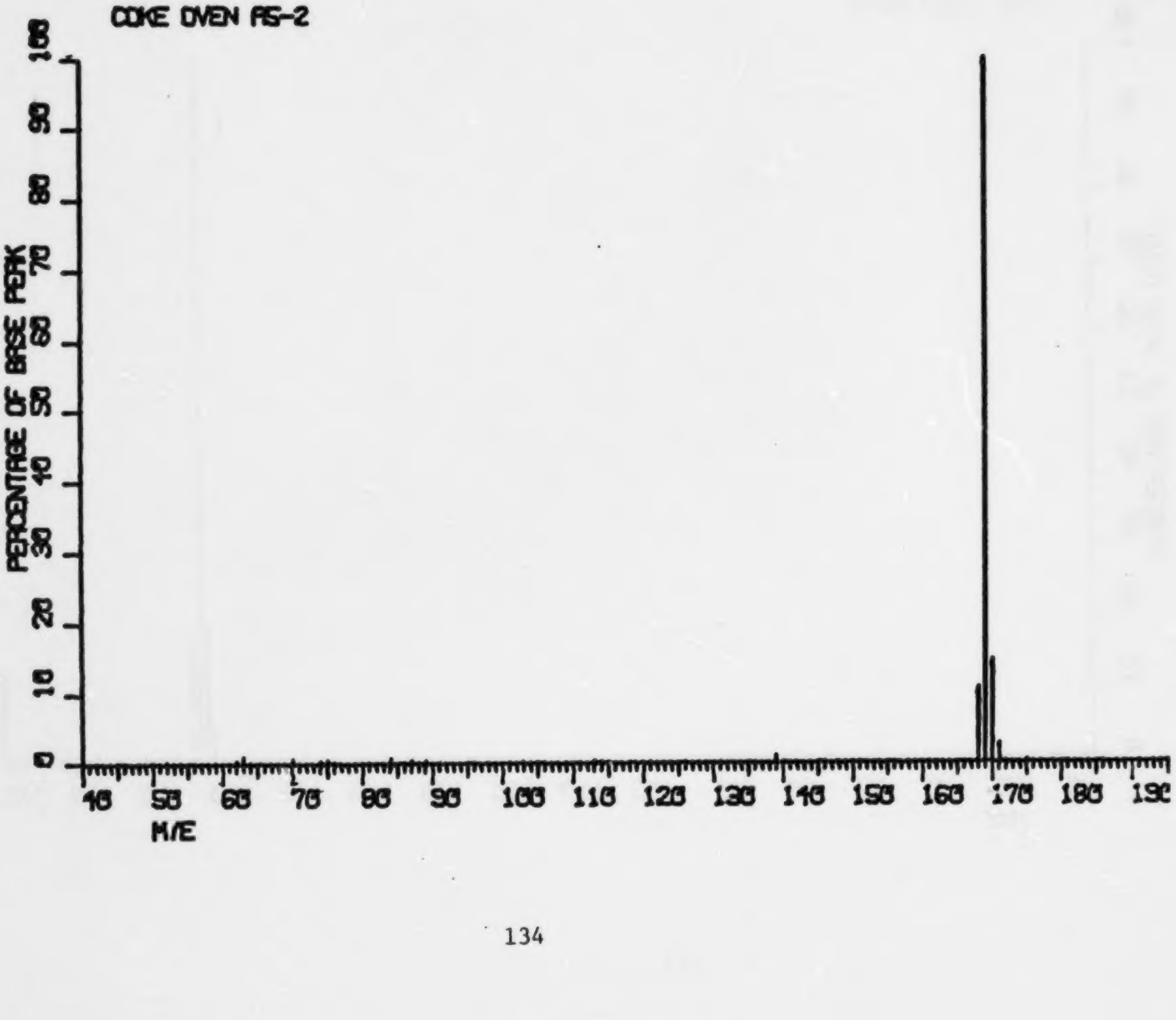
SPECTRUM 83 - 81

COKE OVEN AS-2



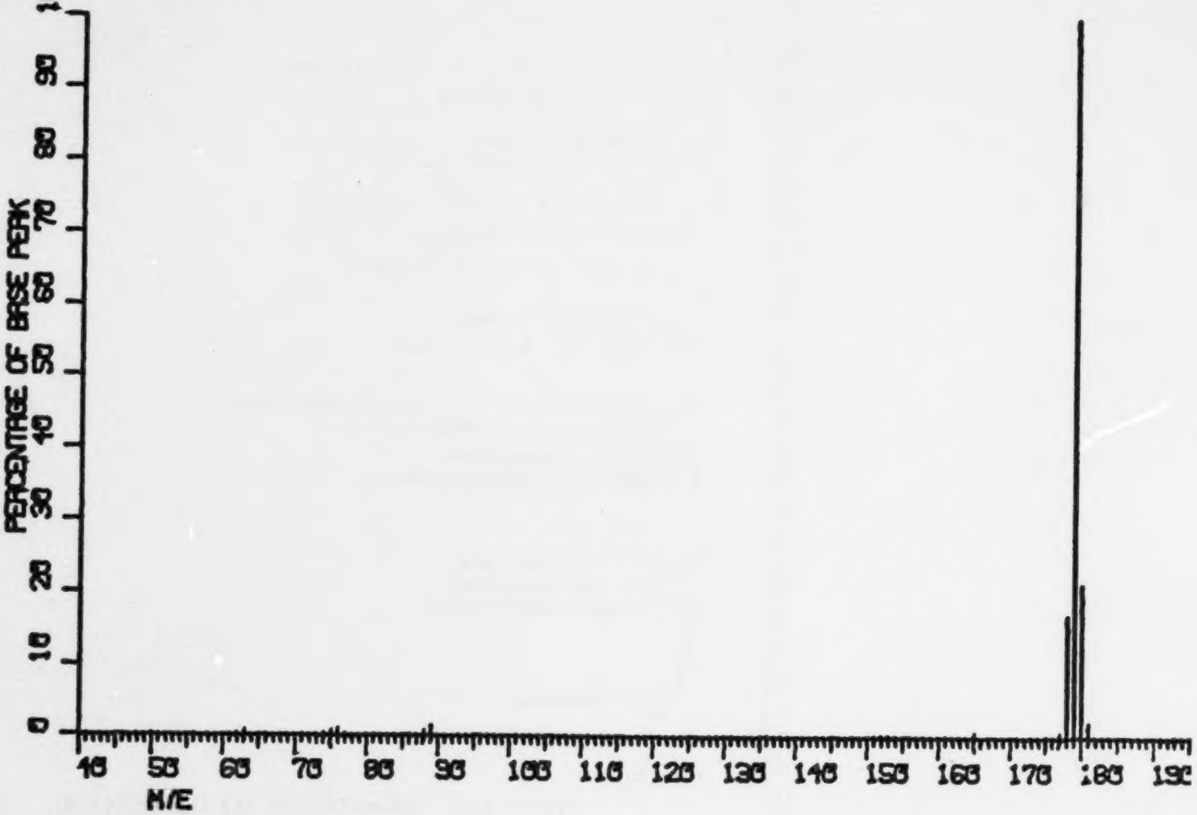
SPECTRUM 71 - 68

COKE OVEN AS-2



SPECTRUM 123 - 127

COKE OVEN AS-2



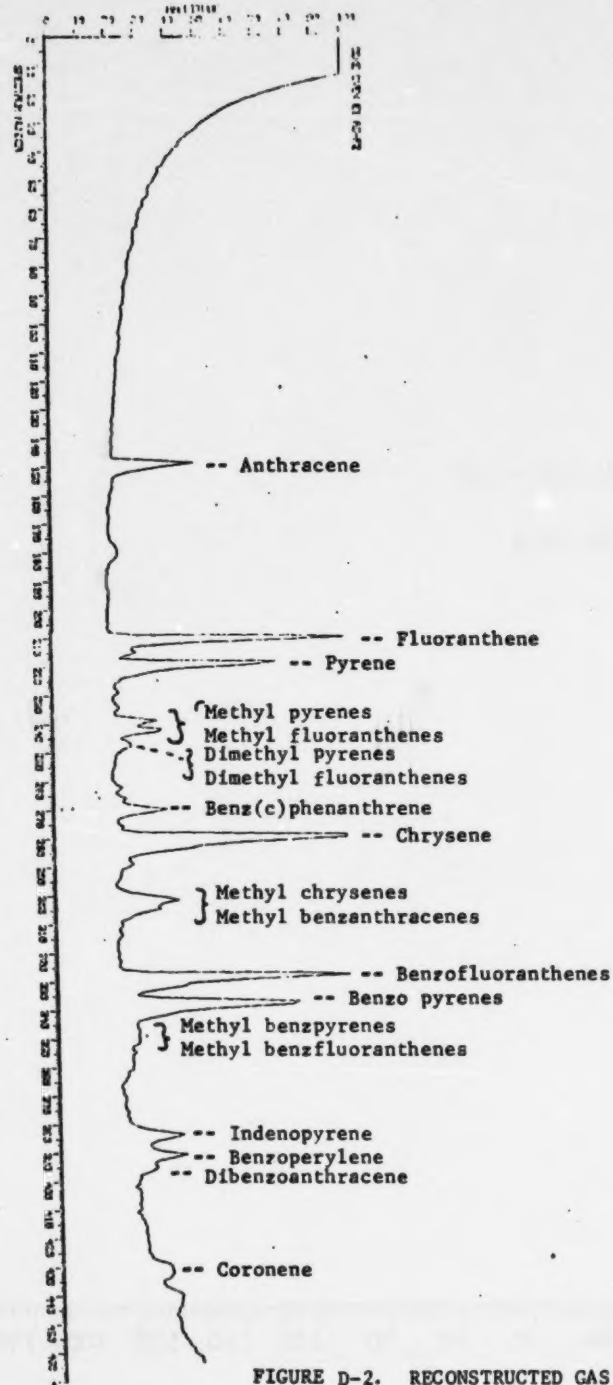
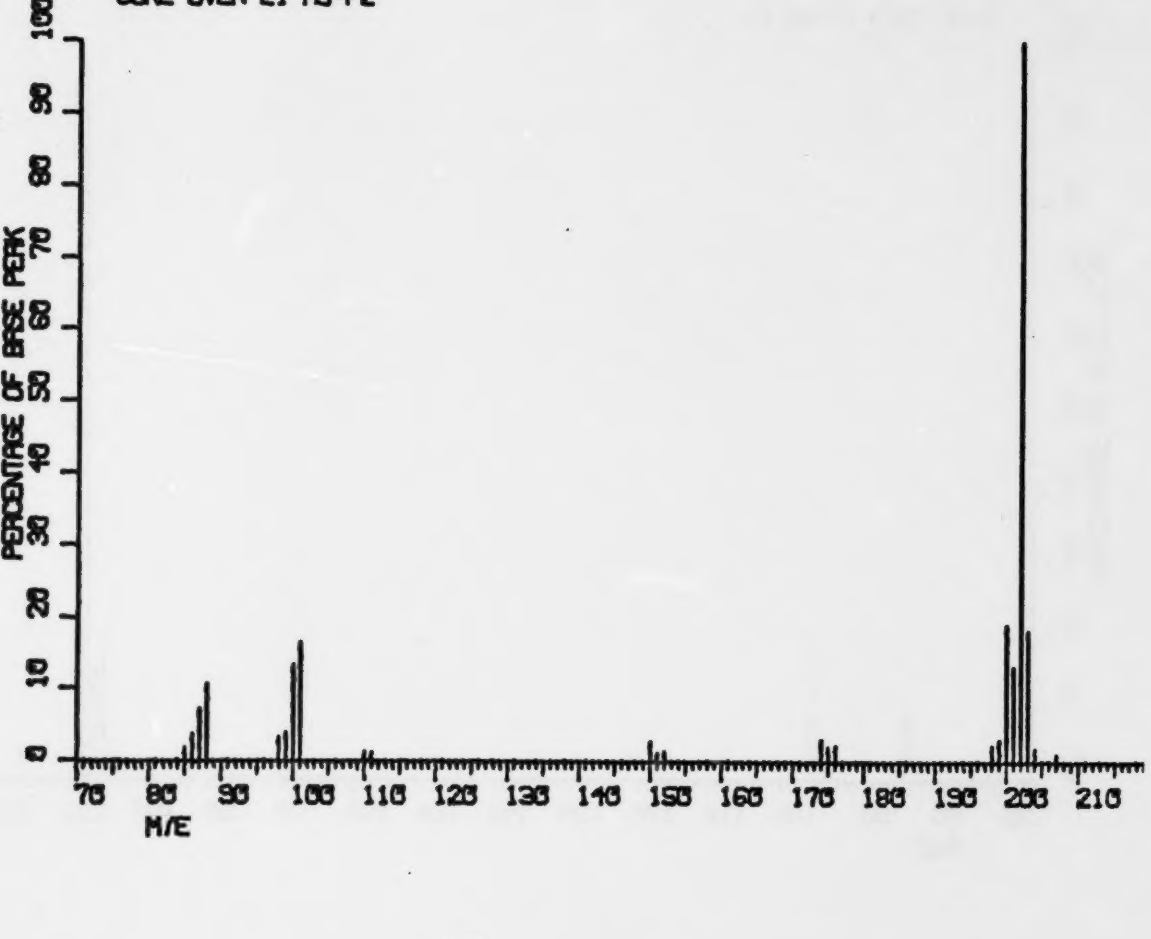
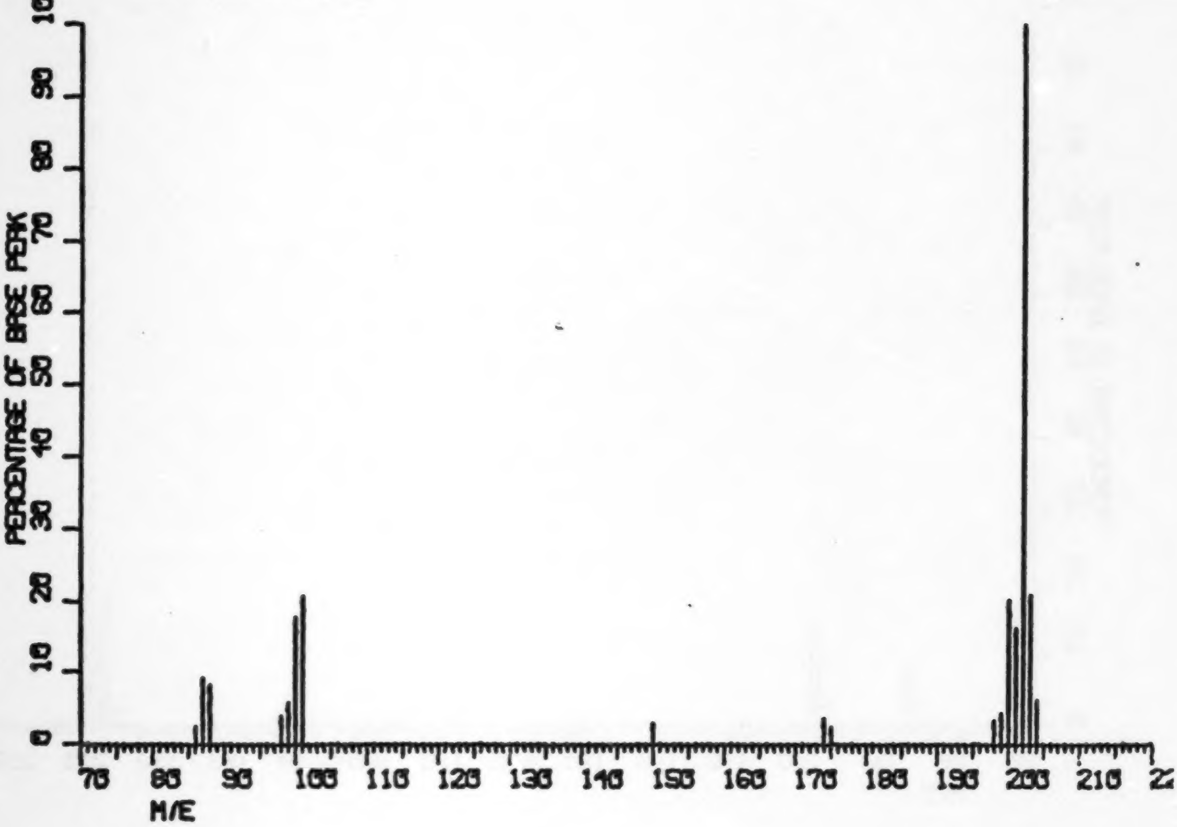


FIGURE D-2. RECONSTRUCTED GAS CHROMATOGRAM; GC-MS ANALYSIS OF COKE OVEN DOOR EMISSIONS, SAMPLE A5F-2

SPECTRUM 211 - 206

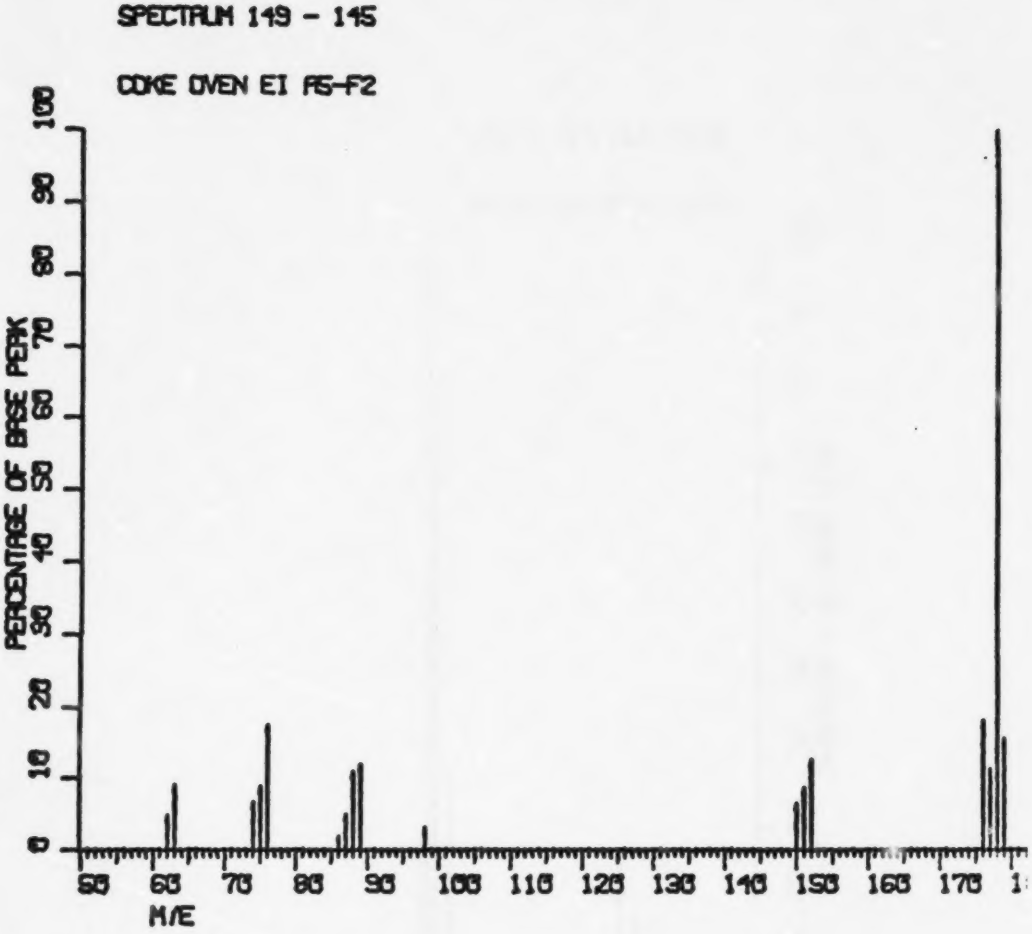
COKE OVEN EI A5-F2





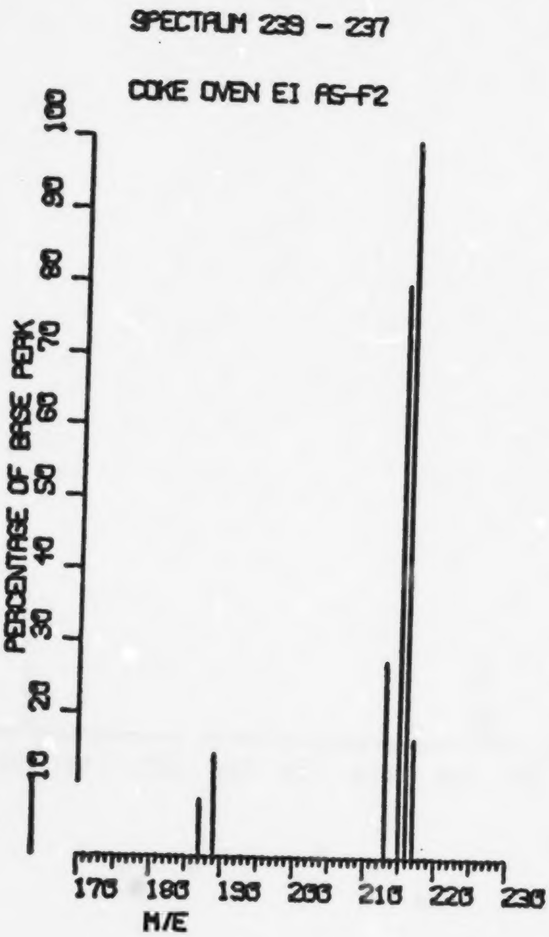
SPECTRUM 220 - 216

COKE OVEN EI AS-F2



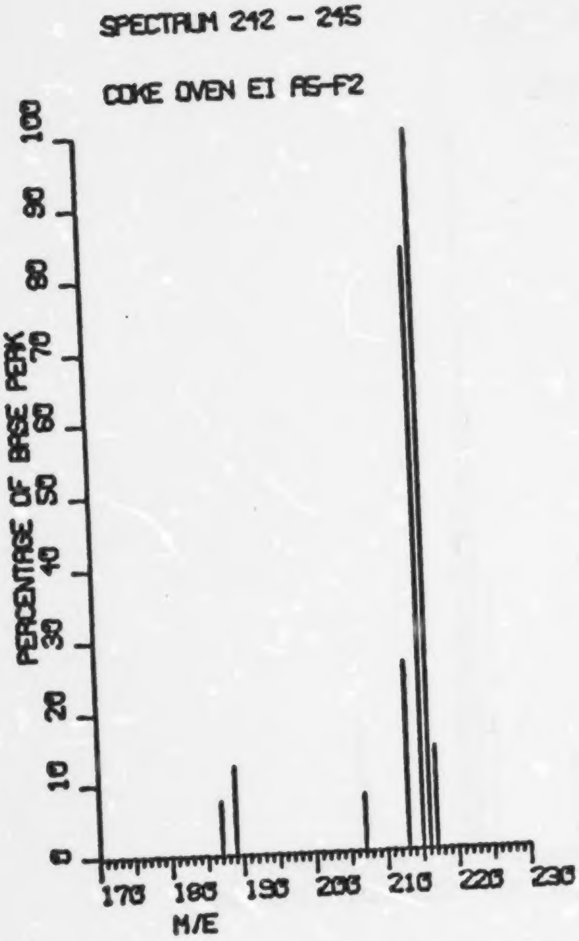
SPECTRUM 149 - 145

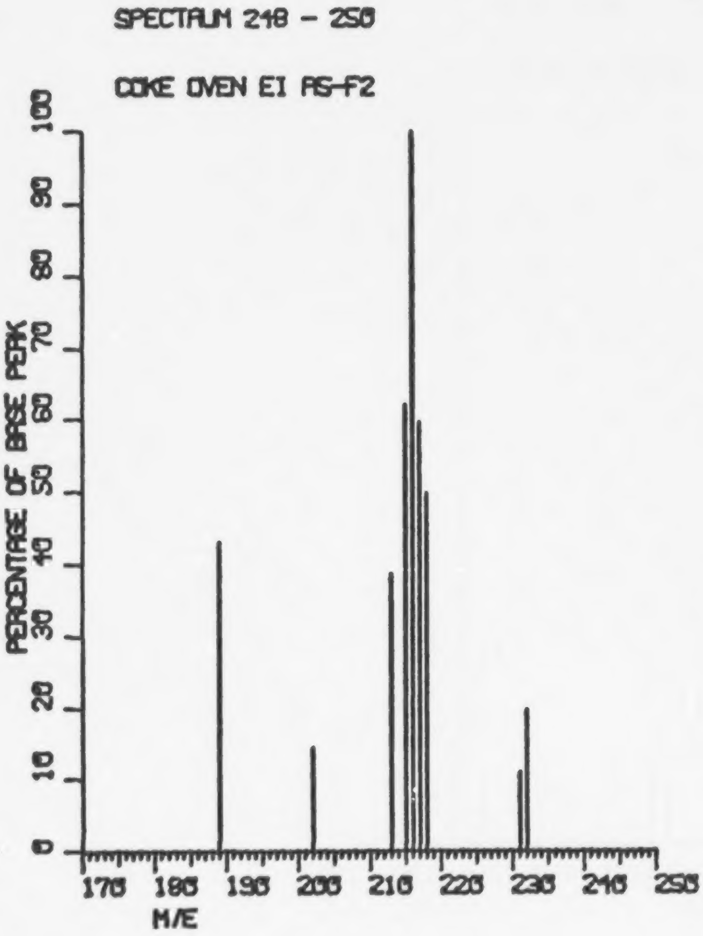
COKE OVEN EI AS-F2



SPECTRUM 239 - 237

COKE OVEN EI AS-F2


SPECTRUM 242 - 245
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
170
180
190
200
210
220
230
M/E


SPECTRUM 248 - 250
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
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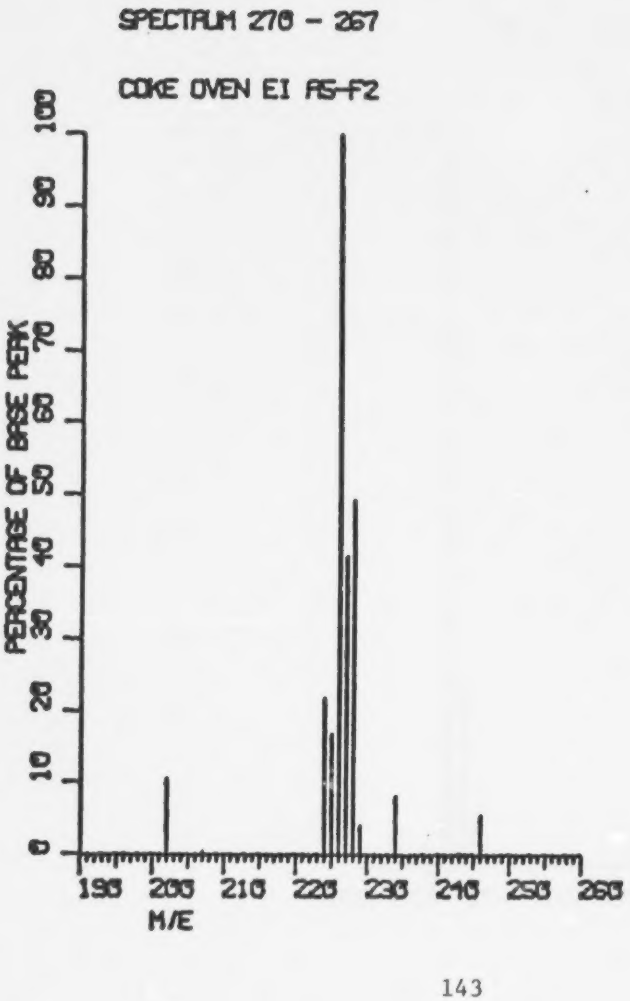
90
100
170
180
190
200
210
220
230
240
250
M/E


SPECTRUM 270 - 267
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
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10
20
30
40
50
60
70
80
90
100
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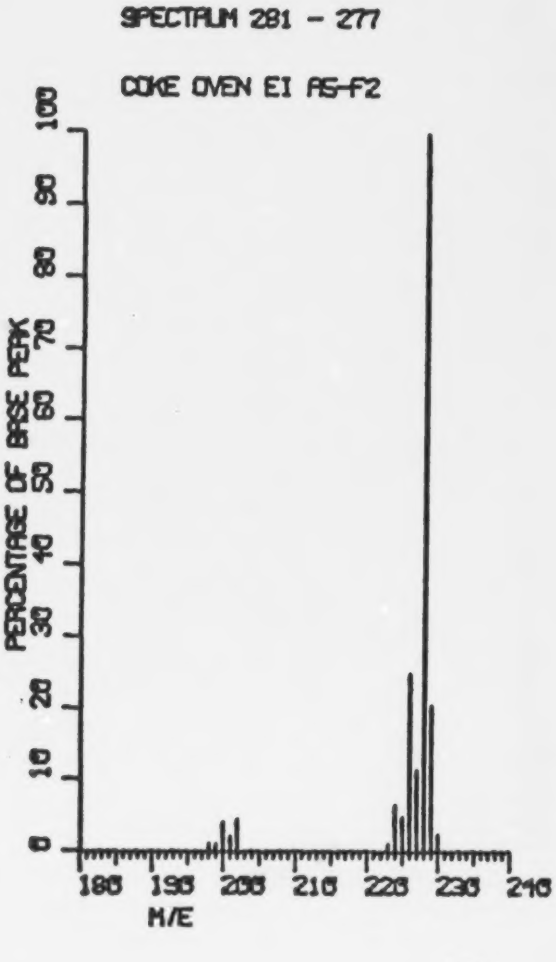
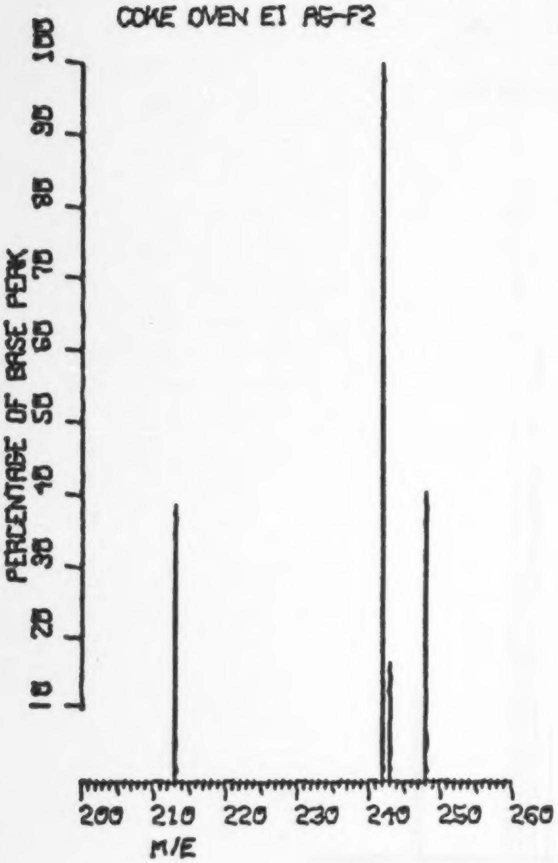
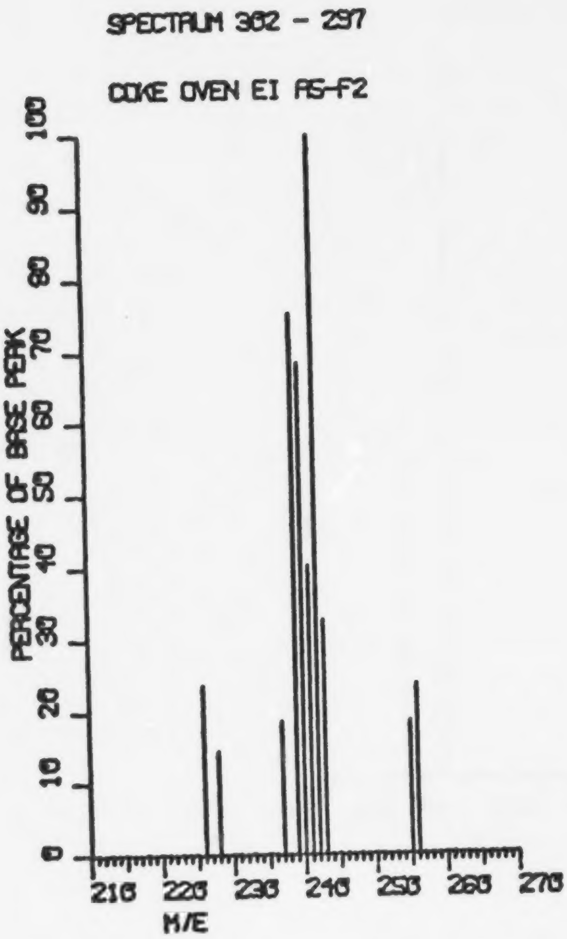
200
210
220
230
240
250
260
M/E


SPECTRUM 281 - 277
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
180
190
200
210
220
230
240
M/E

SPECTRUM 289 - 287

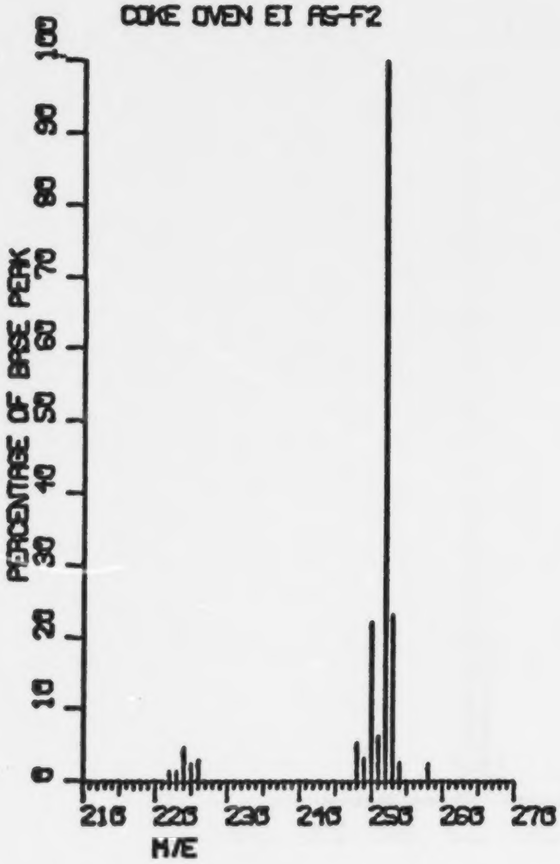
COKE OVEN EI A5-F2

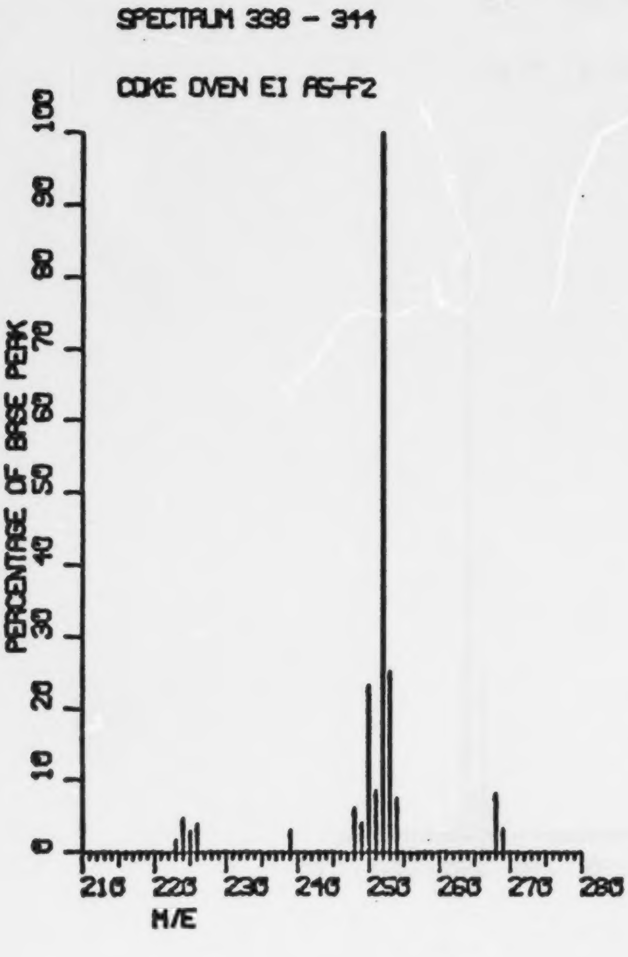



SPECTRUM 302 - 297
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
210
220
230
240
250
260
270
M/E

SPECTRUM 329 - 325

COKE OVEN EI AS-F2




SPECTRUM 338 - 344
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
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100
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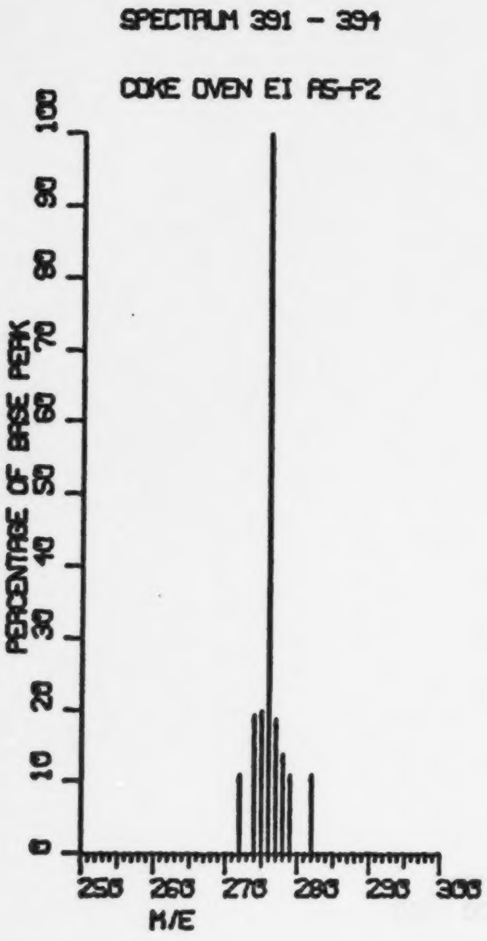
230
240
250
260
270
280
M/E


SPECTRUM 391 - 394
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
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90
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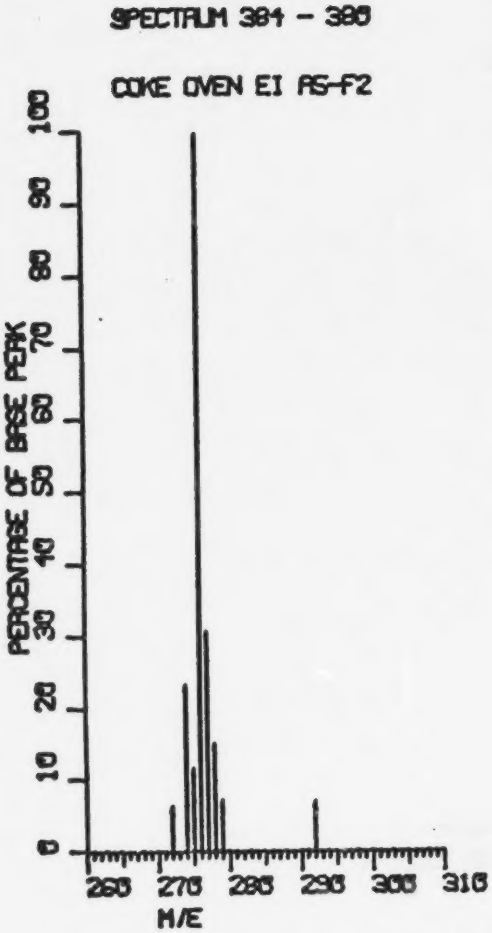
260
270
280
290
300
M/E


SPECTRUM 384 - 380
COKE OVEN EI AS-F2
PERCENTAGE OF BASE PEAK
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10
20
30
40
50
60
70
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90
100
260
270
280
290
300
310
M/E

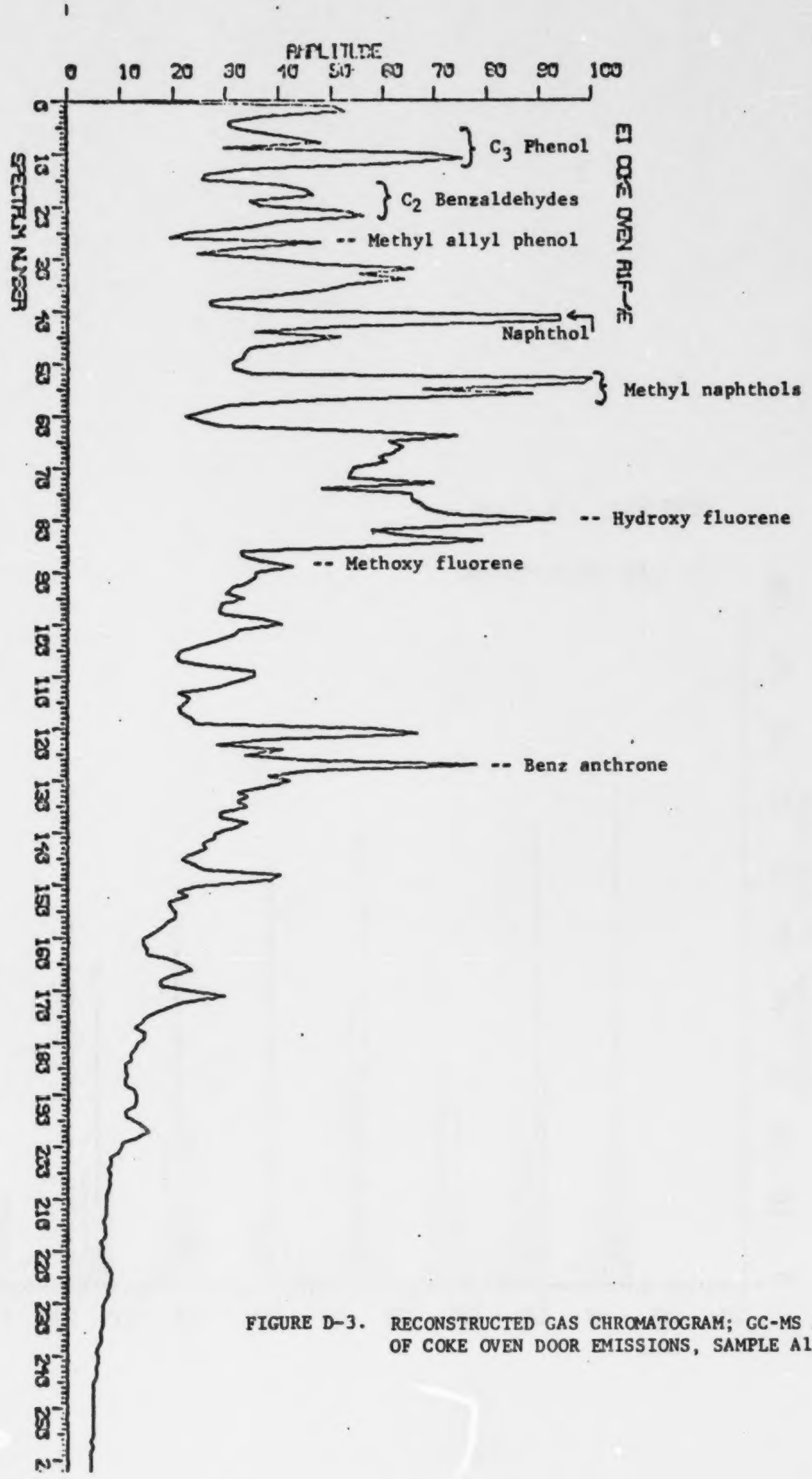
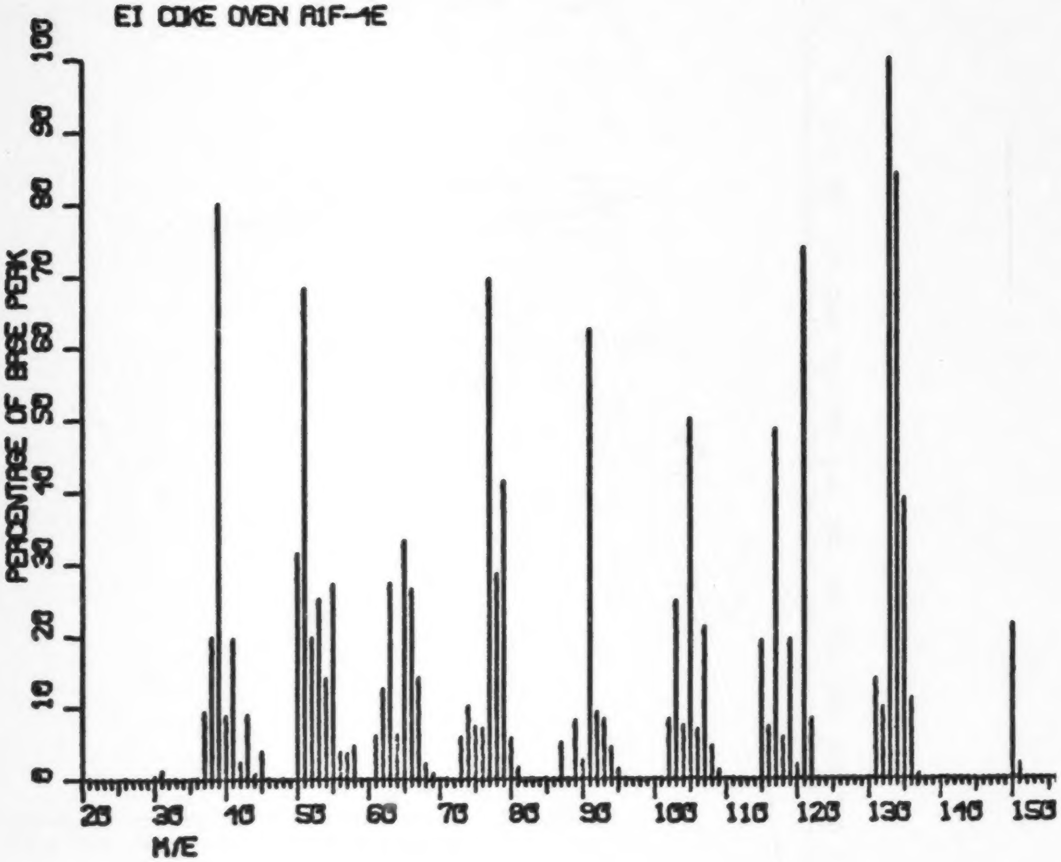


FIGURE D-3. RECONSTRUCTED GAS CHROMATOGRAM; GC-MS ANALYSIS OF COKE OVEN DOOR EMISSIONS, SAMPLE A1F-4

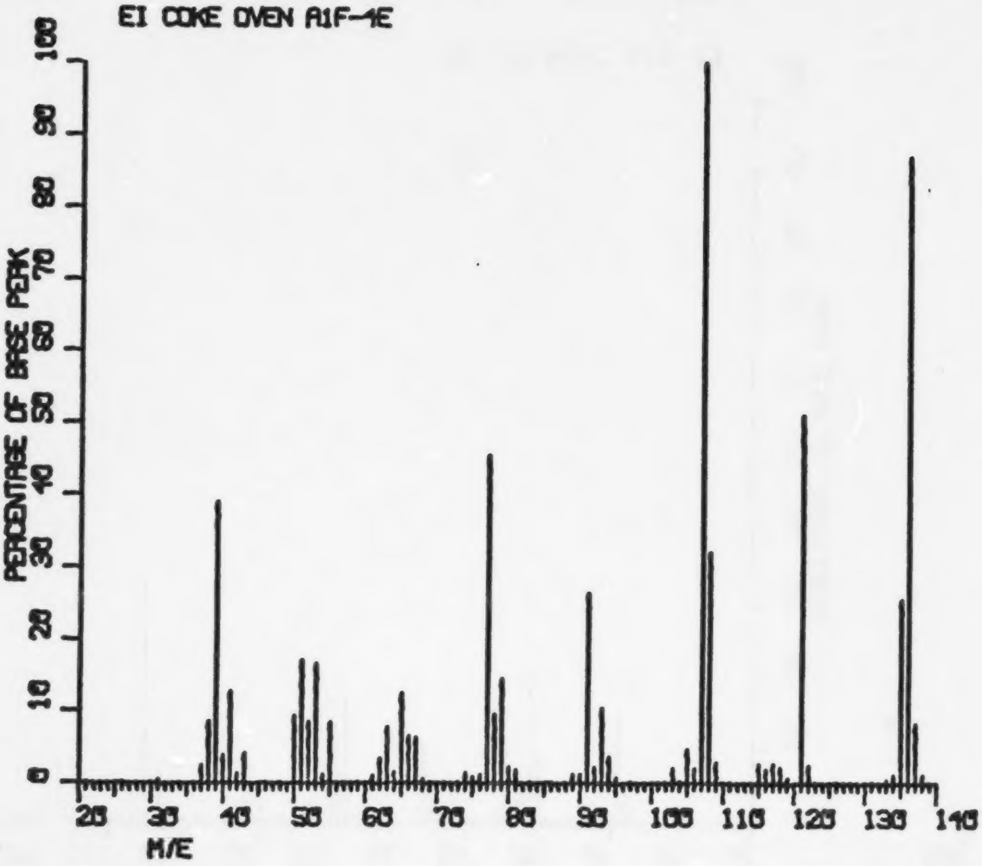
SPECTRUM 18 - 15

EI COKE OVEN A1F-1E



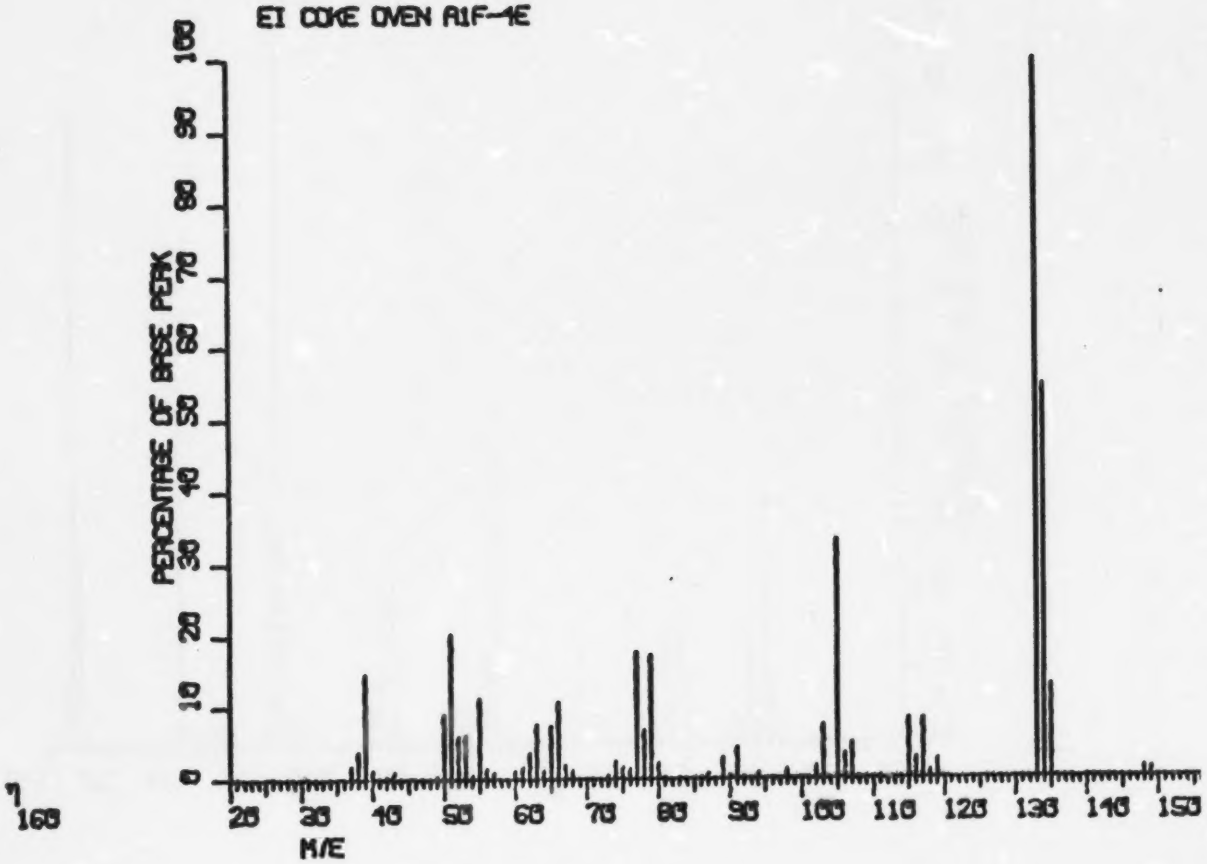
SPECTRUM 11 - 8

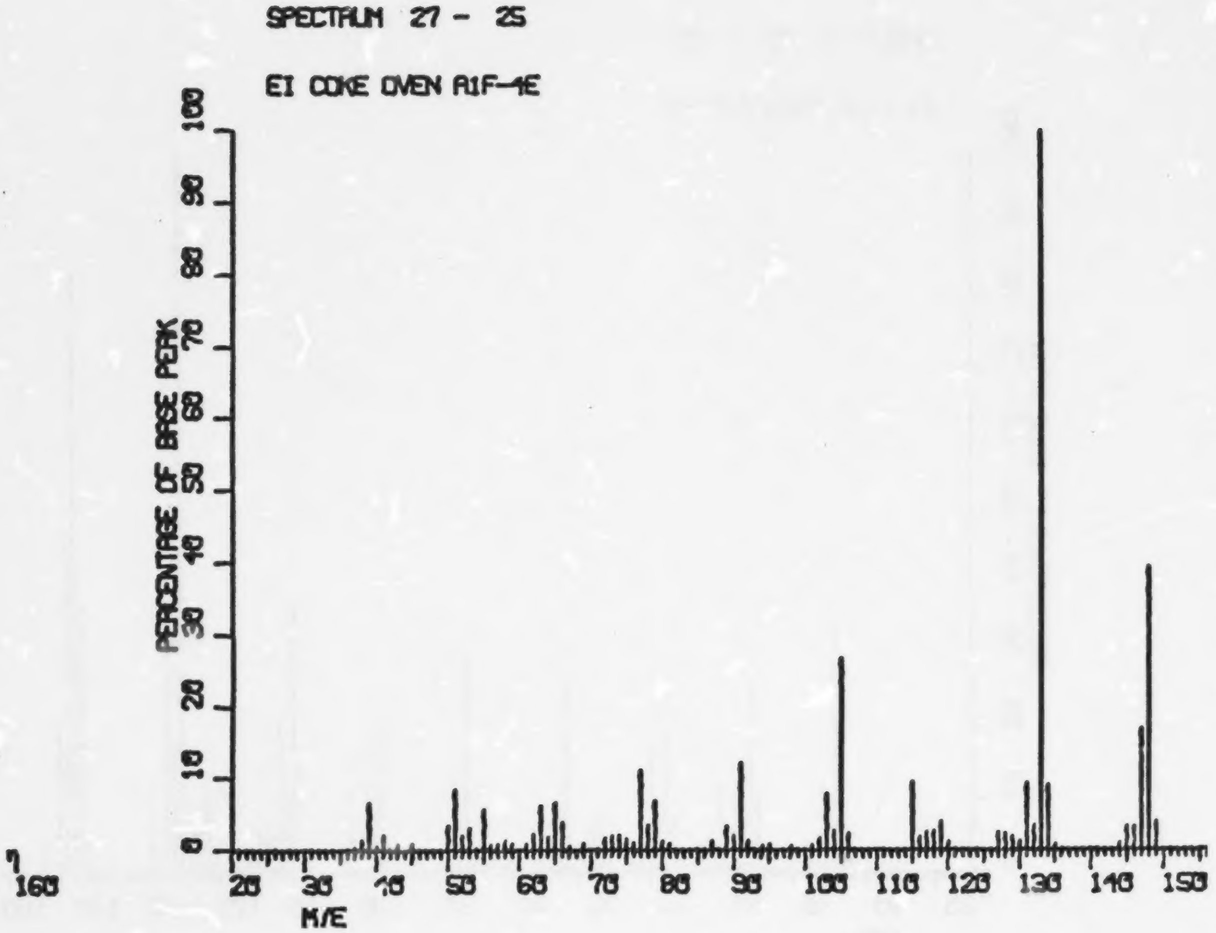
EI COKE OVEN A1F-4E



SPECTRUM 21 - 20

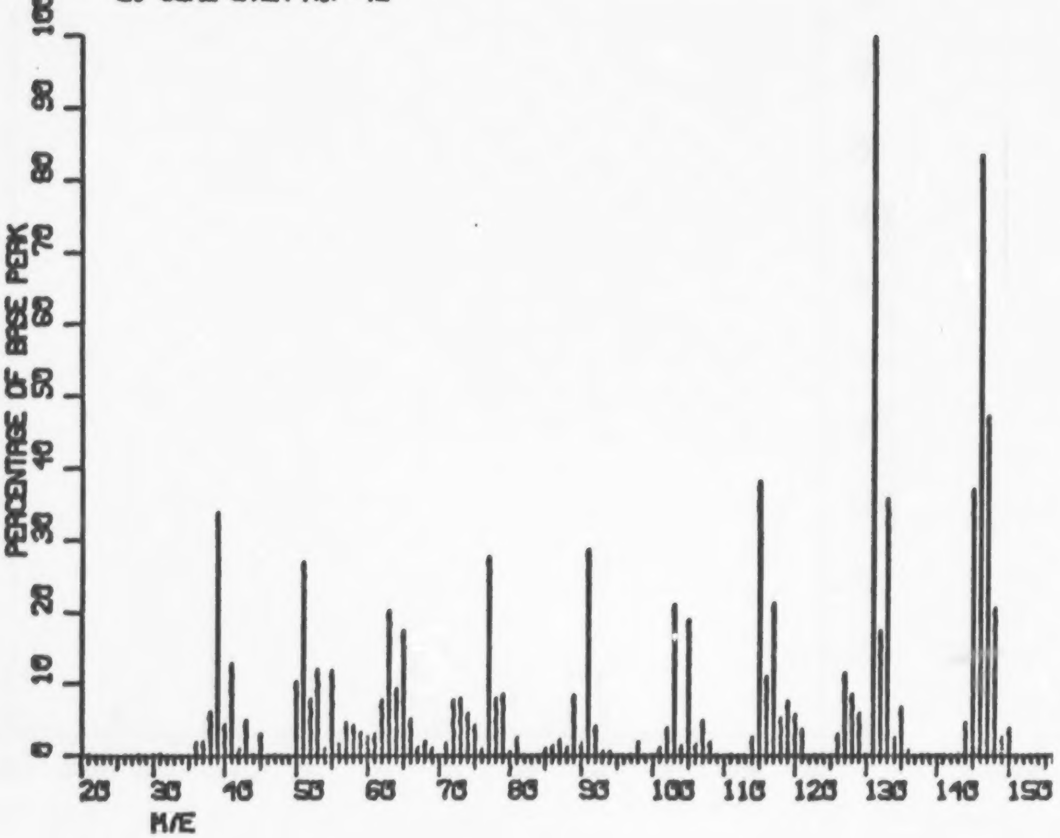
EI COKE OVEN A1F-4E

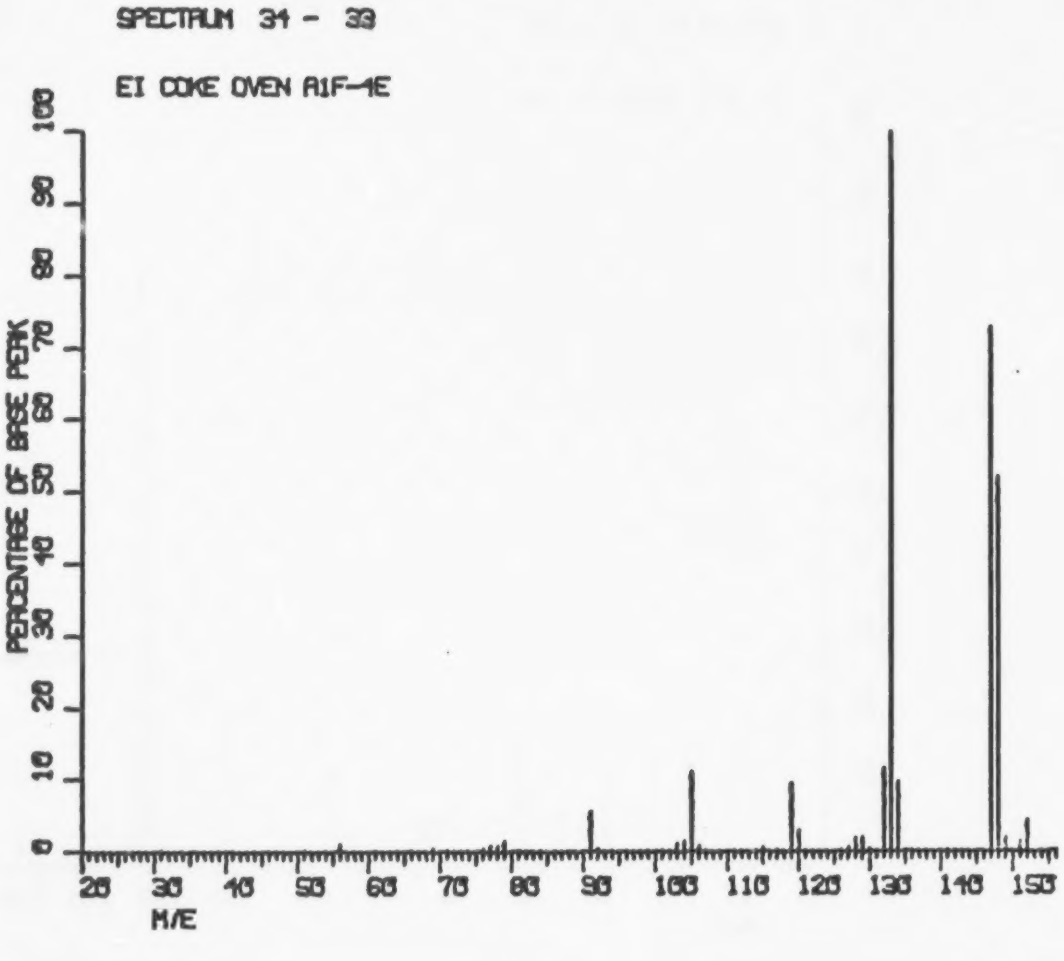



SPECTRUM 27 - 25
EI COKE OVEN A1F-4E
PERCENTAGE OF BASE PEAK
100
90
80
70
60
50
40
30
20
10
0
20
30
40
50
60
70
80
90
100
110
120
130
140
150
M/E
160

SPECTRUM 32 - 30

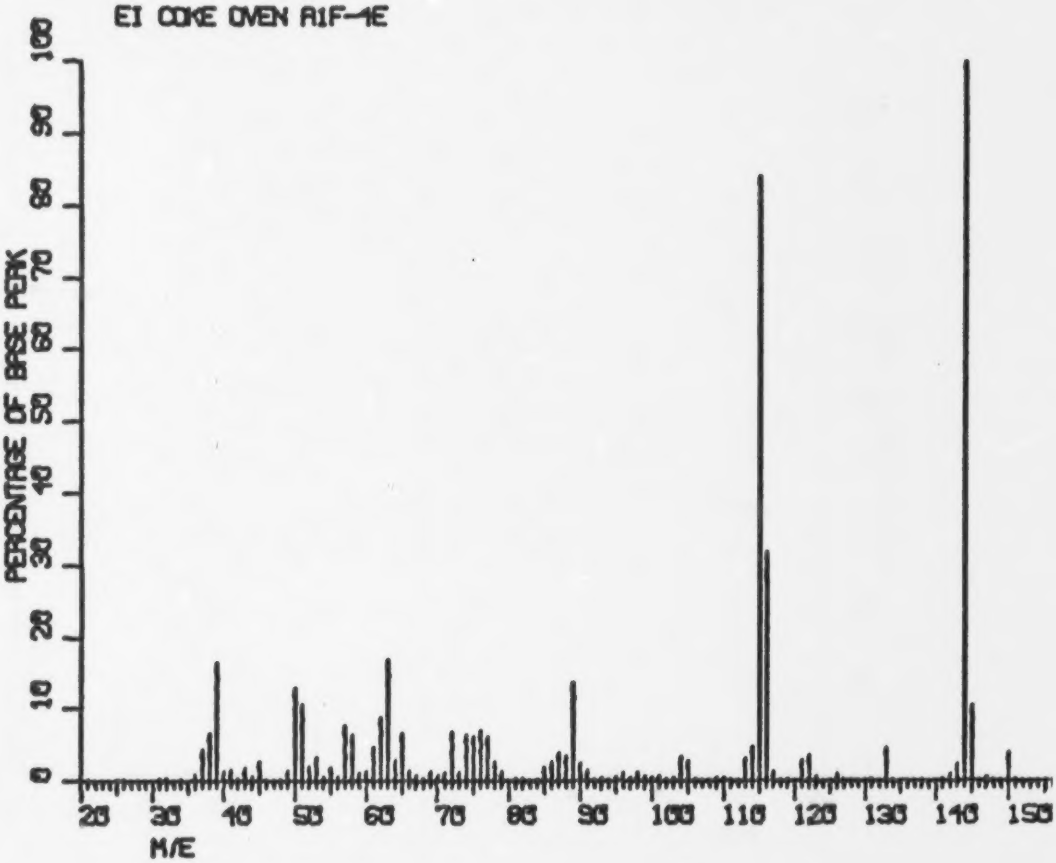
EI COKE OVEN A1F-4E




SPECTRUM 34 - 33
EI COKE OVEN A1F-4E
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
20
30
40
50
60
70
80
90
100
110
120
130
140
150
M/E

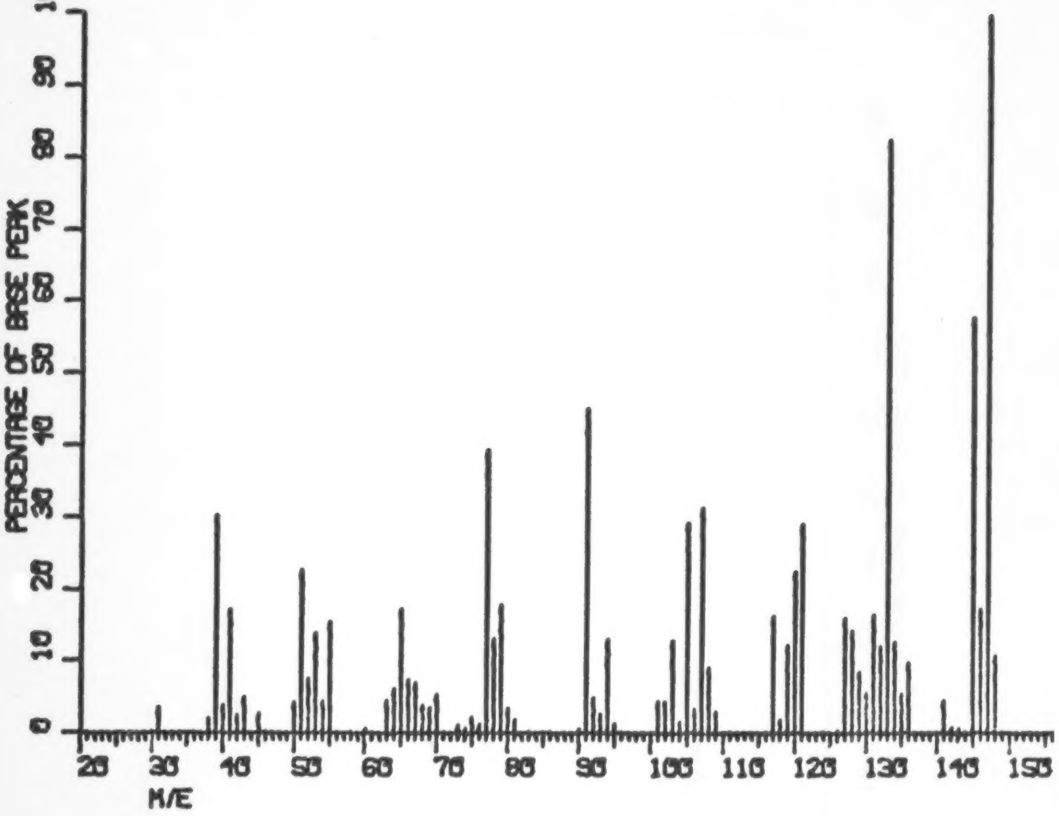
SPECTRUM 42 - 39

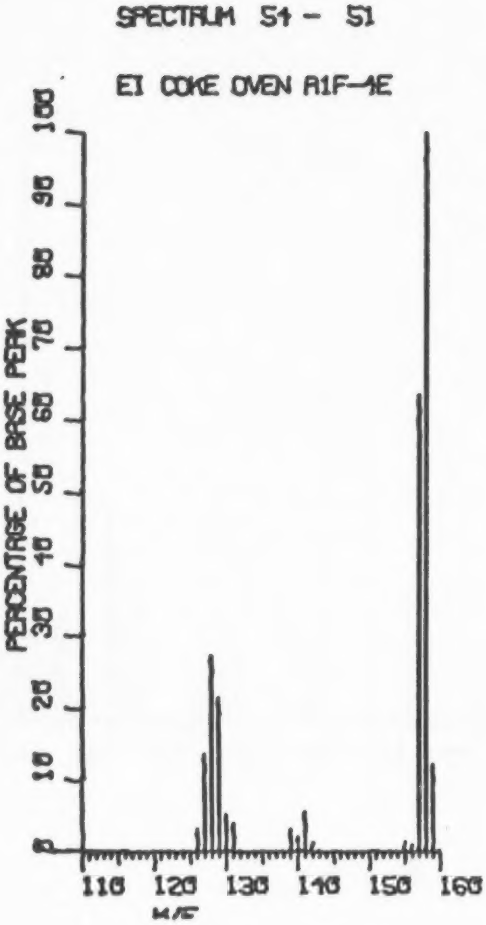
EI COKE OVEN A1F-1E



SPECTRUM 45 - 44

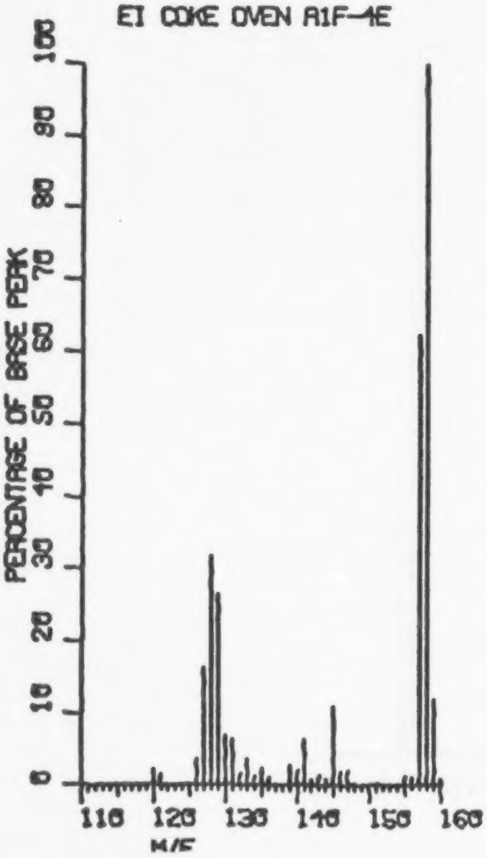
EI COKE OVEN A1F-4E

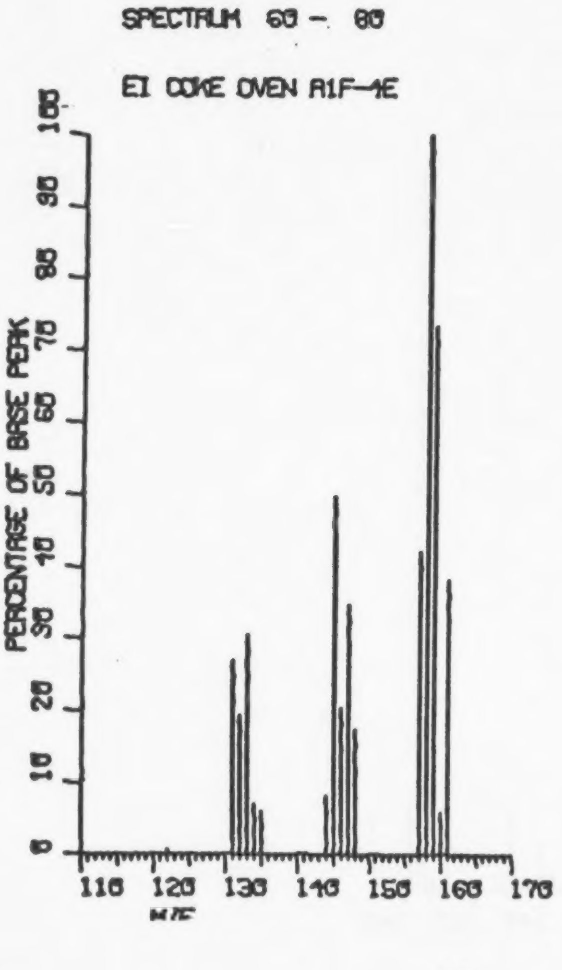


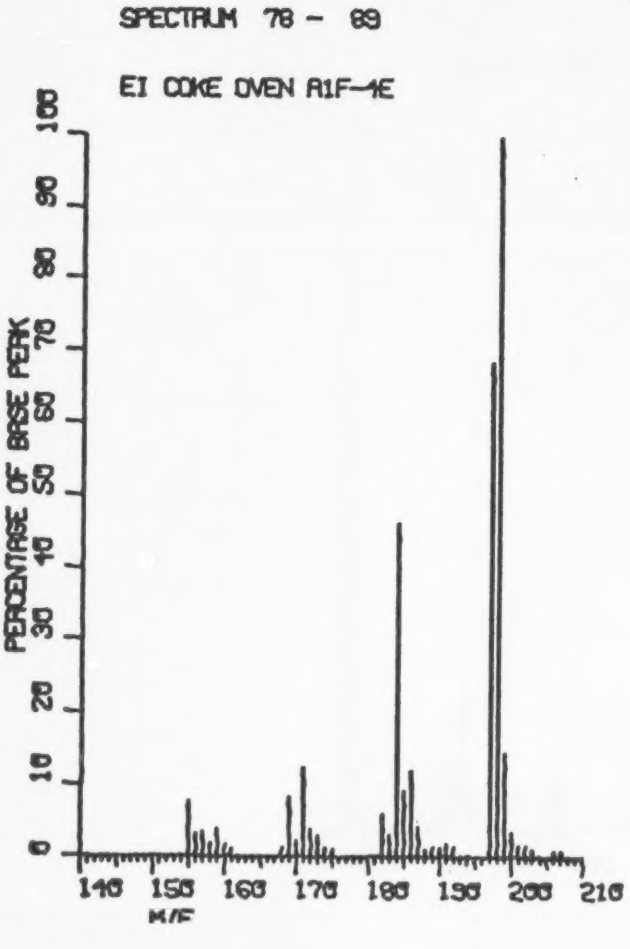

SPECTRUM 54 - 51
EI COKE OVEN A1F-4E
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
M/E

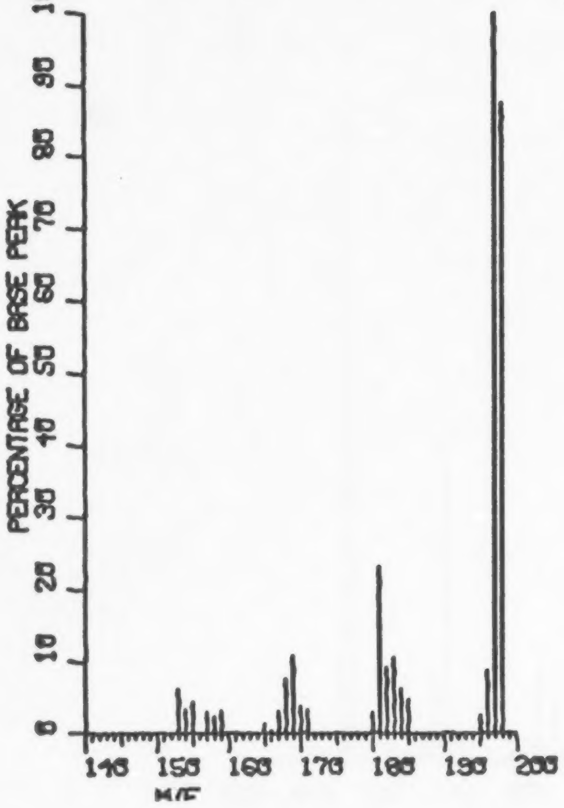
SPECTRUM 56 - 60

EI COKE OVEN A1F-4E



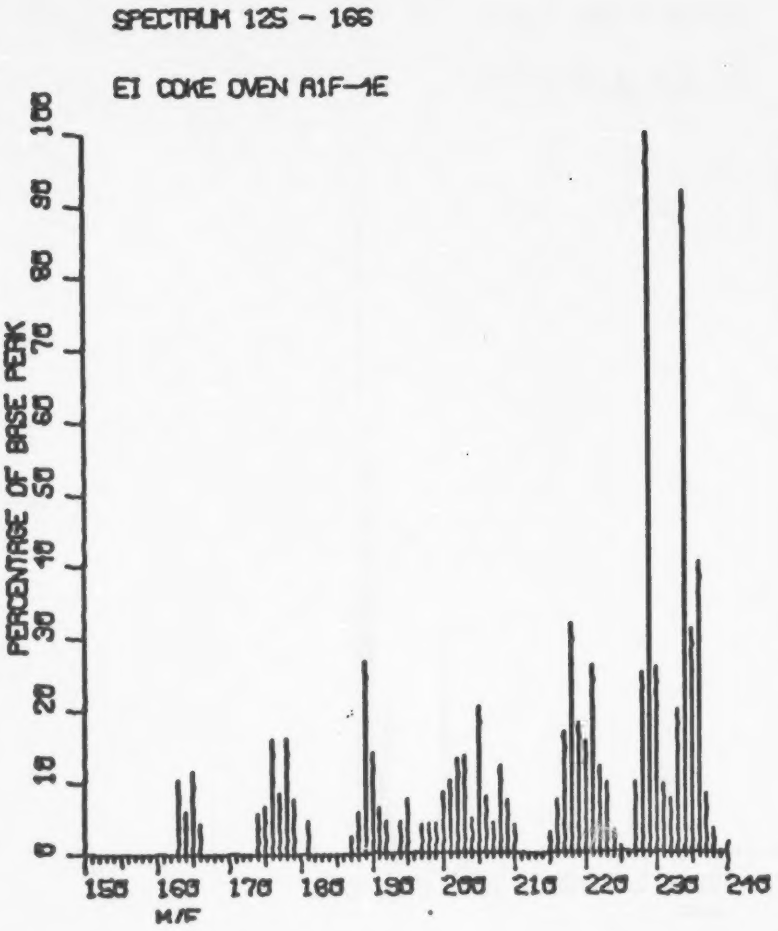

SPECTRUM 60 - 80
EI COKE OVEN A1F-1E
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
M/E


SPECTRUM 78 - 89
EI COKE OVEN A1F-4E
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
140
150
160
170
180
190
200
210
M/E



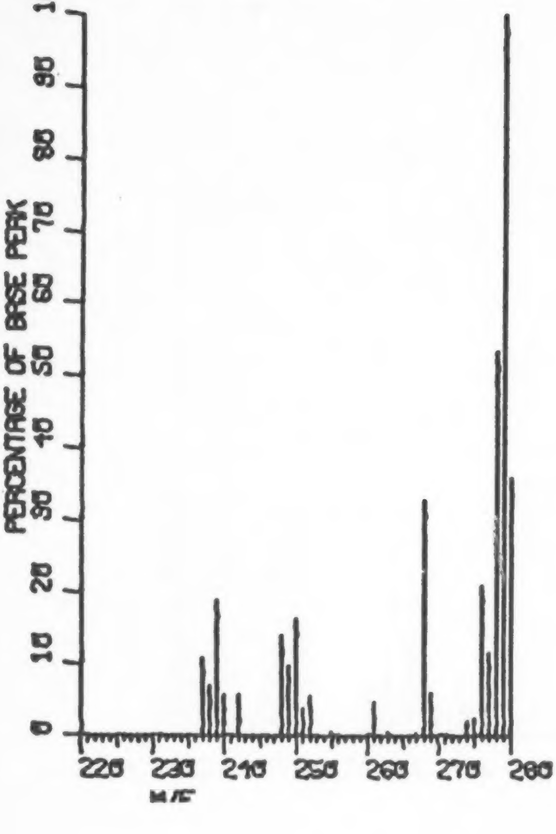
SPECTRUM 87 - 127

EI COKE OVEN A1F-1E


SPECTRUM 125 - 166
EI COKE OVEN A1F-1E
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
150
160
170
180
190
200
210
220
230
240
M/E

SPECTRUM 166 - 163

EI COKE OVEN A1F-4E



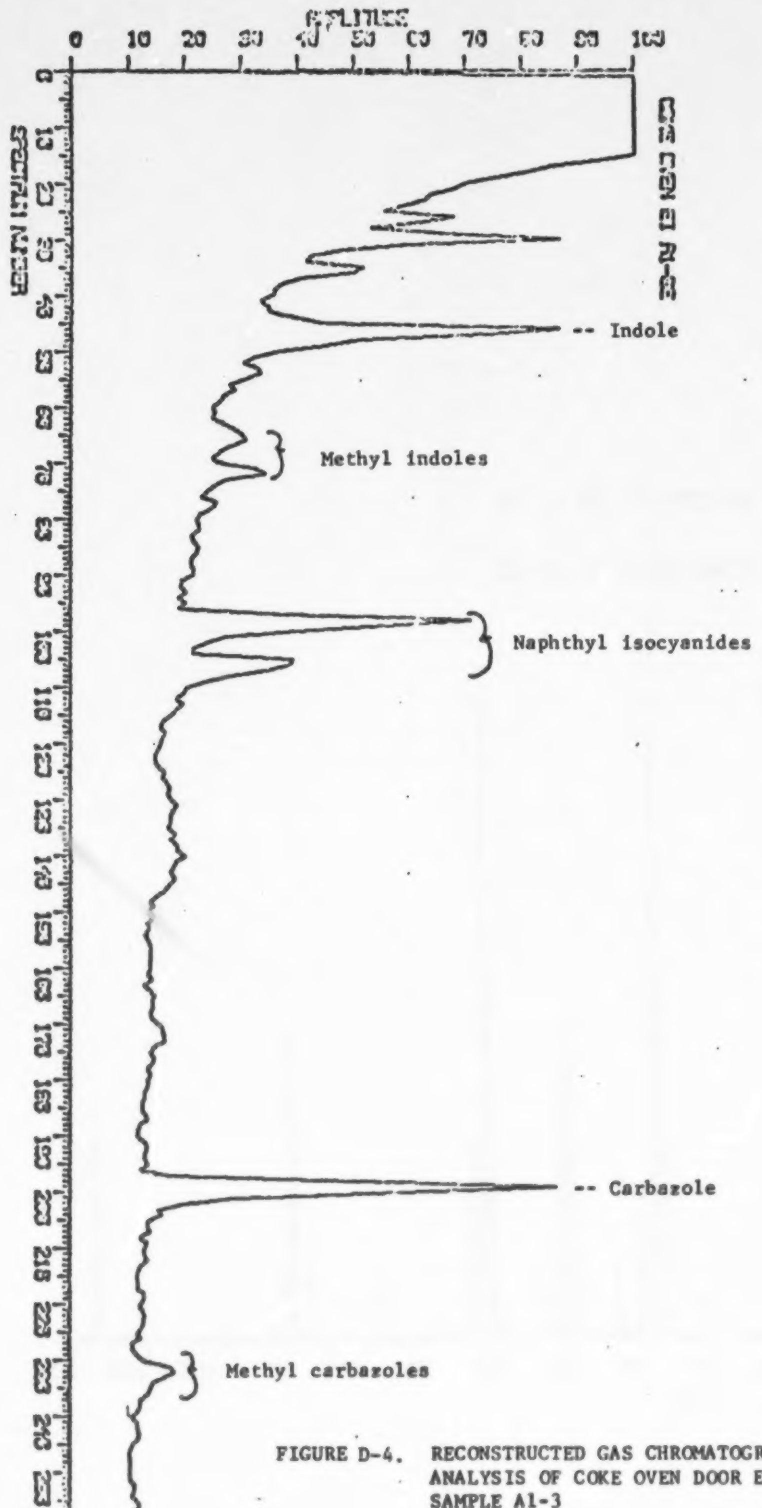
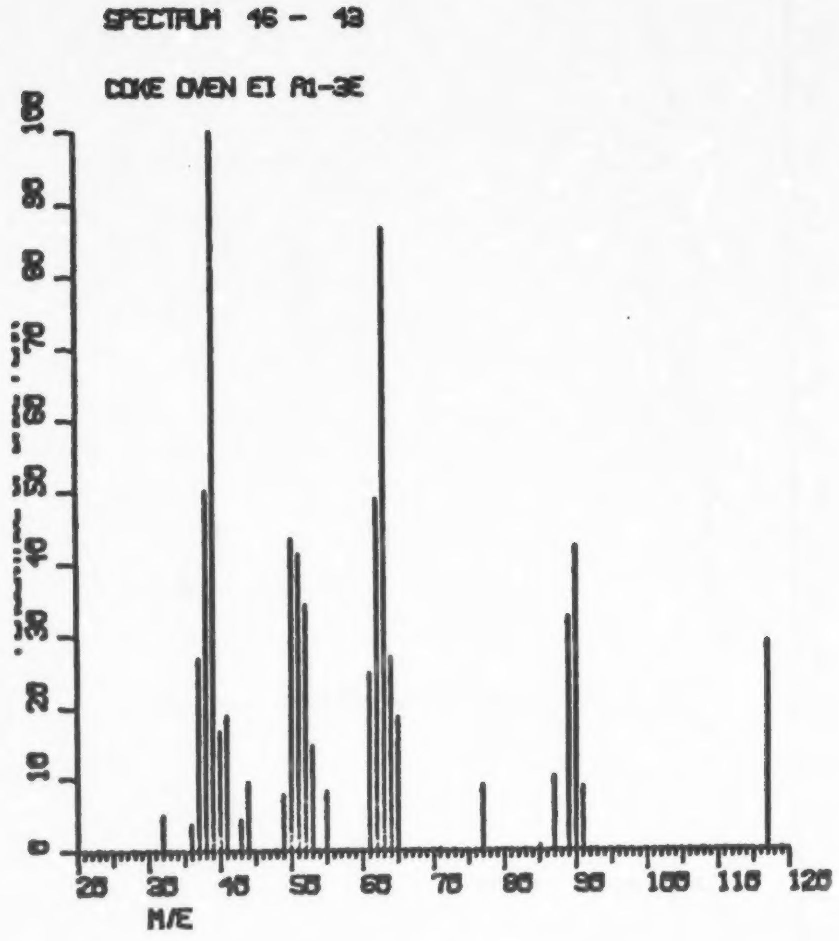


FIGURE D-4. RECONSTRUCTED GAS CHROMATOGRAM; GC-MS ANALYSIS OF COKE OVEN DOOR EMISSION, SAMPLE A1-3

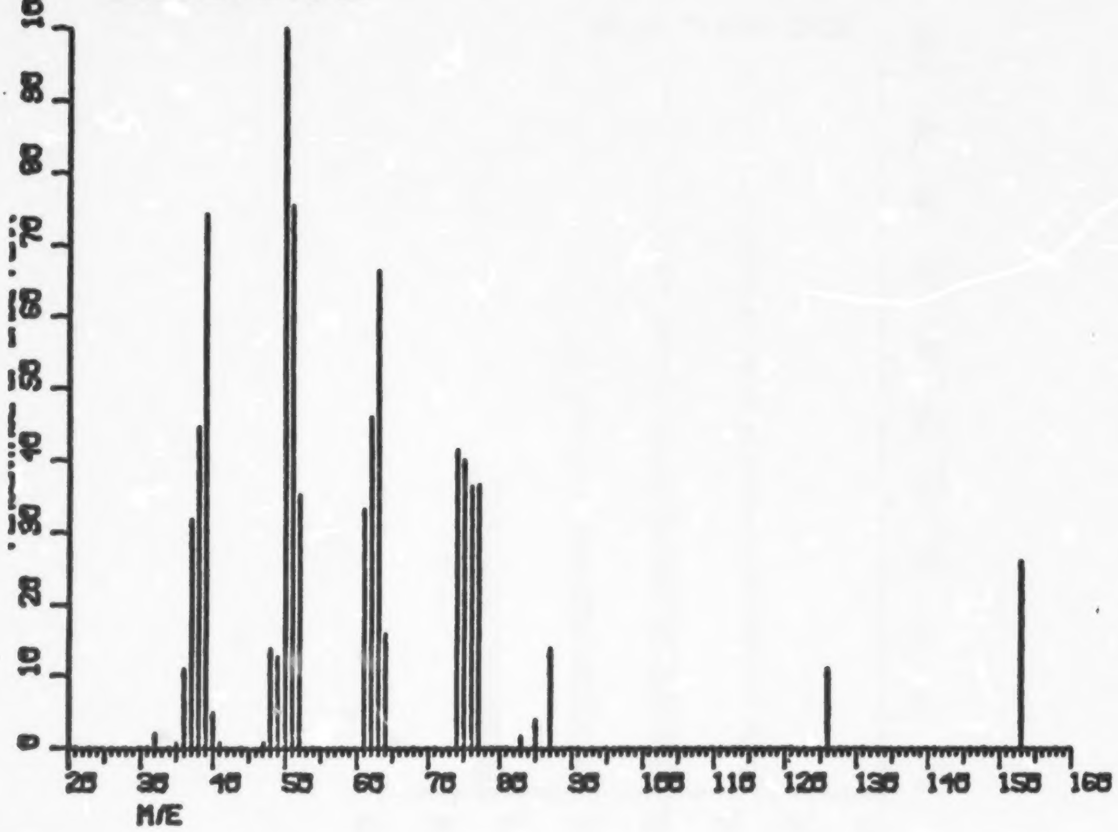


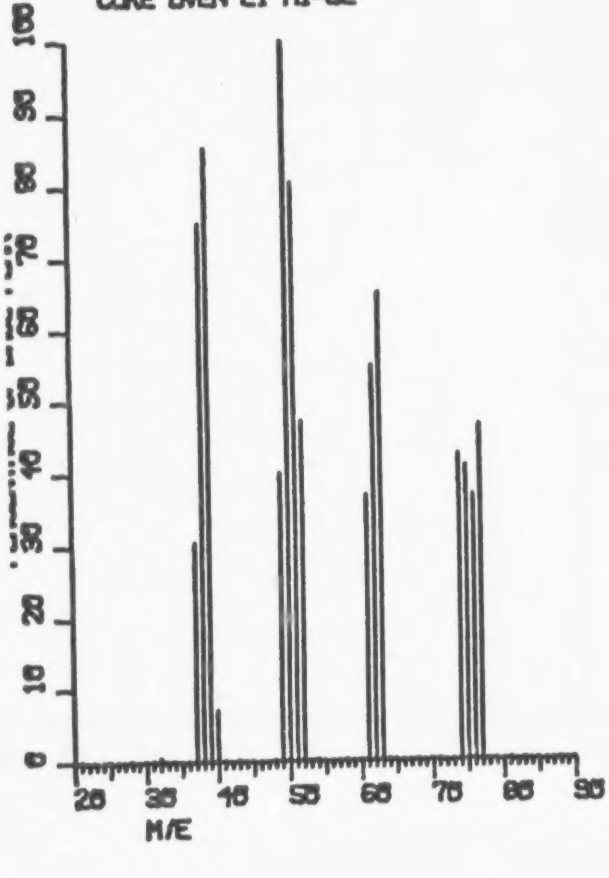
SPECTRUM 46 - 43

COKE OVEN EI A1-3E

SPECTRUM 98 - 182

COKE OVEN EI R1-3E





SPECTRUM 106 - 103

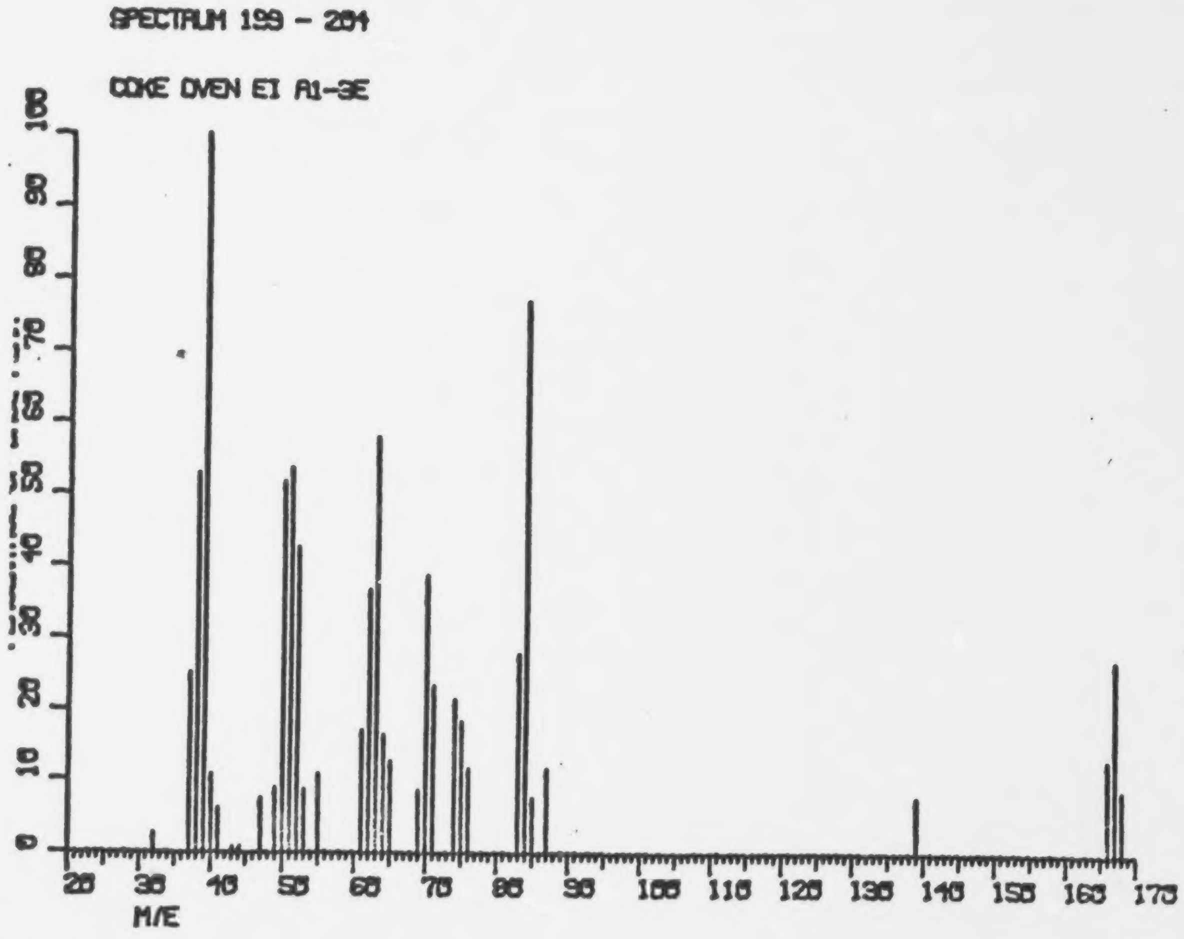
COKE OVEN EI A1-3E

Errata EPA-600/2-77-213

pg. 7 fourth paragraph, second line should read, ".... positive mutagenic response to 0.5 μl of the sample."

pg. 36 (a) second full paragraph, second sentence, Table 1 should be Table 2.

(b) third full paragraph, first sentence should read, ".... is the fact that the average particulate emission rate for Test 2 was 3 times greater than the emission ...."


SPECTRUM 199 - 204
COKE OVEN EI A1-3E
100
90
80
70
60
50
40
30
20
10
0
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
M/E

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16. ABSTRACT
The report gives results of extensive tests of selected fractions of samples of emissions generated by leakage from a coke oven door during a 16-hour coking cycle. The tests included: particulate emissions determination; trace metal analyses; gas analyses; organic analyses by IR spectroscopy, GC-MS, TLC, and HRMS on entire samples or on LC fractions of the samples; and bioassay analyses of bacterial mutagenesis and mammalian cell cytotoxicity. The particulate mass emission determination showed that coke oven emissions can vary considerably from cycle to cycle. The bioassay analyses confirmed that the samples were mutagenic, as implied by the chemical analyses. A sealed hood was fabricated to fit over the coke oven door, so that gases leaking past the door during the coking cycle would be contained and representative samples could be obtained. Additional criteria for the hood included not severely altering the normal door leakage and not interfering with coke oven operation. Initial tests of one hood design suggested modifications which were incorporated into the final design. The final hood was used for conducting two sampling runs at an operating coke oven.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Organic Chemistry	Air Pollution Control	13B	07C
Coking	Bioassay	Stationary Sources	13H	06A
Ovens		Coke Oven Doors	13A	
Leakage		Particulate		
Sampling				
Analyzing				

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